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## CONTENTS.

### PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

	PAGE
LX.—The Constitution of Carbamides. Part VII. The Mechanism of the Synthesis of Urea from the Interaction of Carbonyl Chloride and Ammonia. Part VIII. The Formation of Urea and of Biuret from Oxamide. By EMIL ALPHONSE WERNER and (Part VIII) GEORGE KINGSFORD CARPENTER . . . . .	694
LXI.—A New Method for the Determination of Conductivity. By EDGAR NEWBERRY . . . . .	701
LXII.—The Abnormality of Strong Electrolytes. Part III. The Osmotic Pressure of Salt Solutions and Equilibrium between Electrolytes. By JNANENDRA CHANDRA GHOSH . . . . .	707
LXIII.—The Preparation of certain Organic Stanno- and Stanni-chlorides. By JOHN GERALD FREDERICK DRUCE . . . . .	715
LXIV.—The Basic Carbonates of Copper. By HORACE BARRATT DUNNICLIFF and SUDARSHAN LAL . . . . .	718

## INDEX OF AUTHORS' NAMES.

### IN TRANSACTIONS AND ABSTRACTS.

<p style="text-align: center; margin: 0;"><b>A.</b></p> <p>Acree, S. F. See E. C. White.</p> <p>Addis, T., and A. E. Shevsky, ii, 338, 337.</p> <p>Allen, H. S., ii, 292.</p> <p>Almkvist, G., ii, 320, 333.</p> <p>Amar, J., i, 416.</p> <p>Amberger, C., i, 418.</p> <p>Applebey, M. P., and K. W. Lane, ii, 313.</p> <p>Ariès, E., ii, 294.</p>	<p style="text-align: center; margin: 0;"><b>B.</b></p> <p>Arnold, H., ii, 314.</p> <p>Arnold, R. See H. N. Holmes.</p> <p>Aten, A. H. W., ii, 290.</p> <p>Bachmann, W. See R. Zsigmondy.</p> <p>Baker, J. C. See L. L. van Slyke.</p> <p>Balareff, D., ii, 332.</p>
--	---

Basu, S. N. See M. N. Shaha.  
 Batuecas, T., i, 369.  
 Baumann, L., and H. M. Hines,  
 i, 417.  
 Baur, E., ii, 284.  
 Baxter, G. P., ii, 305.  
 Beckmann, E., R. Paul, and O.  
 Liesche, ii, 308.  
 Berdzeller, L., ii, 340.  
 Bernhard, A., ii, 336.  
 Berthoud, A., ii, 310.  
 Bichowsky, F. R. von, ii, 316.  
 Billeter, O., and B. Wavre, i, 371;  
 ii, 330.  
 Bodenstein, M., ii, 302.  
 Böeseke, J., and C. van Loon,  
 i, 388.  
 Bolin, I., and G. Starck, ii, 334.  
 Born, M., ii, 281, 283.  
 Bosworth, A. W., and L. A. Gib-  
 lin, i, 417.  
 Bousfield, W. R., ii, 293.  
 Boussi, P. See M. Delépine.  
 Braun, J. von, K. Heider, and E.  
 Müller, i, 406.  
 Brecht, J., and M. Savelsberg,  
 i, 382.  
 Brewster, R. Q., i, 393.  
 Briner, E., and E. Fridöri, ii, 302.  
 Brown, H. T., ii, 299.  
 Brûère, P., and E. Chauvenet,  
 ii, 321.  
 Bruins, H. R. See E. Cohen.  
 Brun, A., ii, 323.  
 Butureanu, V. C., ii, 324.

C.

Callisen, K., ii, 326.  
 Carpenter, G. K. See E. A.  
 Werner.  
 Casares, J., and A. Tastet, ii, 330.  
 Cath, P. G., and H. K. Onnes,  
 ii, 291, 294.  
 Chaudhari, T. C., ii, 300.  
 Chaudun, (Mlle.) A. See H. Colin.  
 Chauvenet, E., and (Mlle.) H.  
 Gueylard, ii, 321.  
 Chauvenet, E. See also P.  
 Brûère.  
 Churchill, J. C. See W. R. Ham.  
 Cleage, D. A. See G. T. Morgan.  
 Clifford, W., ii, 314.  
 Cohen, E., ii, 290.  
 Cohen, E., and H. R. Bruins,  
 ii, 297.  
 Colin, H., and (Mlle.) A. Chaudun,  
 i, 414.  
 Compton, A. H., ii, 300.  
 Couderc, V. See V. Thomas.  
 Cunningham, (Miss) M., i, 374.

D.

Dangelmajer, K., ii, 340.  
 Delépine, M., and P. Boussi, ii, 322.  
 Diels, O., and H. Roehling, i, 400.  
 Druce, J. G. F., TRANS., 715.  
 Du Bois E. M. See J. Tambor.  
 Dunncliff, H. B., and S. Lal.  
 TRANS., 718.  
 Duret, P., ii, 335.

E.

Edlbacher, S., ii, 336.  
 Eggert, J., i, 369.  
 Eichel, A. See K. Hess.  
 Eismayer, K. See T. Zincke.  
 Ellis, M. T., i, 420.  
 Ephraim, F., ii, 313.  
 Ephraim, F., and E. Rosenber,  
 i, 389.  
 Euler, H. von, i, 414.  
 Everest, A. E., i, 420.

F.

Fehrle, H., ii, 296.  
 Feulgen, R., i, 413.  
 Fichter, F., and E. Krummer-  
 acher, i, 369.  
 Fleck, E. H. See J. Piccard.  
 Foote, H. W. See H. L. Wells.  
 Foote, P. D. See J. T. Tata.  
 Fort, C. A. See V. J. Harding.  
 Foshag, W., ii, 324.  
 Fowler, A., ii, 281.  
 Fowler, A., and C. C. L. Gregor;  
 ii, 282.  
 Francesco, M., ii, 340.  
 Freudenberg, K., i, 403.  
 Fridöri, E. See E. Briner.  
 Fuchs, P., ii, 298.

G.

Gassmann, T., ii, 309.  
 Ghosh, J. C., TRANS., 707.  
 Giblin, L. A. See A. W. Bo-  
 worth.  
 Graham, R. P. D., ii, 324.  
 Graham, R. P. D. See also J.  
 Poitevin.  
 Gregory, C. C. L. See A. Fowler.  
 Groschuff, E., ii, 322.  
 Grossfeld, J., ii, 337.  
 Grüneisen, E., ii, 287.  
 Gueylard, (Mlle.) H. See E. Cha-  
 venet.  
 Guye, P. A., and F. Schneide  
 ii, 310.

**H.**

- Haarmann, R. See C. Harries.  
 Haas, A. R. C., i, 412.  
 Hackh, I. W. D., ii, 306.  
 Hale, W. J., and F. C. Vibrans, i, 380.  
 Haller, A., and J. Louvrier, i, 397.  
 Ham, W. R., J. C. Churchill, and H. M. Ryder, ii, 292.  
 Hamburger, L. See W. Reinders.  
 Hantzsck, A., ii, 299.  
 Harding, V. J., and C. A. Fort, i, 417.  
 Harries, C., and R. Haarmann, ii, 296.  
 Hartmann, W. See C. Paal.  
 Hedvall, J. A., ii, 320.  
 Heider, K. See J. von Braun.  
 Herz, W., ii, 292.  
 Herzfeld, K. F., ii, 289.  
 Hess, K., i, 403, 404.  
 Hess, K., and A. Eichel, i, 404.  
 Hess, K., and F. Leibbrandt, i, 401.  
 Hettner, G., ii, 282.  
 Hill, C. A. See H. D. Richmond.  
 Hines, H. M. See L. Baumann.  
 Hirschberg, E., i, 416.  
 Hirschberg, E., and H. Winterstein, i, 416.  
 Hodgkinson, W. R., i, 381.  
 Hönig, M., and J. Spitzer, i, 375.  
 Hofmann, A. See H. Meyer.  
 Hoffmann, K. A., and H. Schibsted, ii, 329.  
 Holmes, H. N., and R. Arnold, ii, 317.  
 Holtsmark, J., ii, 283.  
 Honda, K., and T. Murakami, ii, 316.

**I.**

- Itallic, L. van, i, 419.

**J.**

- Jänecke, E., ii, 313.  
 Jamieson, G. S., ii, 335.  
 Jaquet, D. See R. Willstätter.

**K.**

- Karrer, P. See A. Werner.  
 Kharasch, M. See J. Piccard.  
 Kiplinger, C. C., ii, 294.  
 Kirchhof, F., ii, 300.  
 Knight, N. See D. M. Torrance.  
 Knoop, F., i, 412.  
 Kohlweiler, E., ii, 286, 304.

- Kondō, K. See K. Ōshima.  
 Konek, F. von, ii, 309.  
 Konek, F. von, and R. Mitterhauser, i, 408.  
 Konek, F. von, and E. Pacsu, i, 394.  
 Konek, F. von, and O. Schleifer, i, 407.  
 Kornfeld, G. See V. Rothmund.  
 Kraemer, G., ii, 331.  
 Krause, E., i, 415.  
 Kroo, J., ii, 303.  
 Krummenacher, E. See F. Fichter.  
 Kruyt, H. R., ii, 289.

**L.**

- Laar, J. J. van, ii, 291.  
 Lacroix, A., ii, 324.  
 Lal, S. See H. B. Dunnieliff.  
 Lane, K. W. See M. P. Applebey.  
 Larsen, L. M. See J. Piccard.  
 Le Bas, G., ii, 281, 292.  
 Leibbrandt, F. See K. Hess.  
 Leśnianski, W. S., i, 405.  
 Lewcock, W., i, 382.  
 Lewis, H. F., ii, 333.  
 Lieb, H. See A. Zinke.  
 Liesche, O. See E. Beckmann.  
 Loeb, J., i, 413.  
 Loon, C. van. See J. Böeseken.  
 Lopez Peréz, L., i, 417.  
 Lorenz, R., ii, 303.  
 Loring, F. H., ii, 291.  
 Louvrier, J. See A. Haller.

**M.**

- Macht, D. L., i, 418.  
 Madinaveitia, A., and J. Puyal, i, 373.  
 Madinaveitia, A., and J. Ranedo, i, 415.  
 Maggi, H., and C. Woker, i, 375.  
 Maignon, F., i, 416.  
 Mailhe, A., i, 389.  
 Martin, E., ii, 330.  
 Matignon, C., and F. Meyer, ii, 302.  
 Matissen, S. See A. Werner.  
 Maue, G., ii, 336.  
 Maxted, E. B., ii, 310.  
 Merrill, G. F., ii, 323.  
 Meyer, F. See C. Matignon.  
 Meyer, H., and A. Hofmann, i, 383.  
 Meyer, J., ii, 292.  
 Michaud, F., ii, 293.  
 Mitterhauser, R. See F. von Konek.  
 Moeller, W., ii, 301.

Monhaupt, M., ii, 335.  
 Moore, F. J., and R. M. Thomas,  
 i, 410.  
 Moreau-Talon, (Mlle.) A. See A.  
 Villiers.  
 Morgan, G. T., and D. A. Cleage,  
 i, 411.  
 Morrell, R. S., i, 372.  
 Mottram, V. H., ii, 338.  
 Mügge, O., ii, 313.  
 Müller, A., i, 382.  
 Müller, E. See J. von Braun.  
 Murakami, T. See K. Honda.

## N.

Neun, D. E. See H. C. Sherman.  
 Newbery, E., TRANS., 701.  
 Niggli, P., ii, 315.  
 Nomura, H., i, 396.

## O.

Ohlon, S. E., ii, 285.  
 Onnes, H. K. See P. G. Cath.  
 Öryng, T., ii, 317.  
 Oshima, K., and K. Kondō, i, 419;  
 ii, 338.  
 Owen, E. A., ii, 284.

## P.

Paal, C., and W. Hartmann, ii, 303.  
 Pacsu, E. See F. von Konek.  
 Paneth, F., ii, 304, 305.  
 Papish, J., ii, 309.  
 Paul, B. See E. Beckmann.  
 Petrie, J. M., i, 420.  
 Petterson-Björck, L., i, 371.  
 Pfeiffer, P., i, 389.  
 Piccard, J., M. Kharasch, and  
 E. H. Fleck, i, 385.  
 Piccard, J., and L. M. Larsen,  
 i, 396.  
 Pinkus, A., ii, 286.  
 Pinnow, J. See L. Wolfrum.  
 Poitevin, E., and R. P. D. Gra-  
 ham, ii, 323.  
 Porter, A. W., ii, 296.  
 Prior, G. T., ii, 326, 327.  
 Puyal, J. See A. Madinaveitia.

## R.

Rahlén, E. See A. Windaus.  
 Rai, H., ii, 310.  
 Ranedo, J., i, 388.  
 Ranedo, J. See also A. Madina-  
 veitia.

Reinders, W., and L. Hamburger,  
 ii, 312.  
 Reitsstötter, J. See A. Westgren.  
 Richmond, H. D., and C. A. Hill,  
 ii, 339.  
 Roehling, H. See O. Diels.  
 Rosenberg, E. See F. Ephraim.  
 Rothmund, V., and G. Kornfeld,  
 ii, 315.  
 Ruff, O., ii, 314.  
 Ruoss, H., ii, 337.  
 Ruzicka, L., i, 398.  
 Ryder, H. M. See W. R. Ham.

## S.

Sanchez, J. A., ii, 340.  
 Sarasin, J., i, 375.  
 Savelsberg, M. See J. Bredt.  
 Schaefer, C., and M. Schubert,  
 ii, 282, 315.  
 Schall, C., i, 389.  
 Schibsted, H. See K. A. Hof-  
 mann.  
 Schimank, H., ii, 296.  
 Schleifer, O. See F. von Konek.  
 Schmidt, C., ii, 305.  
 Schneider, F. See P. A. Guye.  
 Schroeter, G., and K. Thomas,  
 i, 418.  
 Schubert, M. See C. Schaefer.  
 Schudel, G. See R. Willstätter.  
 Shaha, M. N., and S. N. Basu,  
 ii, 291.  
 Shannon, E. V., ii, 323.  
 Sherman, H. C., and D. E. Neun,  
 i, 414.  
 Shevsky, A. E. See T. Addis.  
 Shibko, J., ii, 334.  
 Slyke, L. L. van, and J. C. Baker,  
 i, 413, 417.  
 Smith, L., i, 370.  
 Sommerfeld, A., ii, 303.  
 Sonn, A., i, 401.  
 Spitzer, J. See M. Hönig.  
 Stahrross, K., ii, 312.  
 Starck, G. See I. Bollin.  
 Strecker, W., ii, 332.

## T.

Tambor, J., and E. M. Du Bois,  
 i, 395.  
 Tastet, A. See J. Casares.  
 Tate, J. T., and P. D. Foote, ii, 287.  
 Thomas, K. See G. Schroeter.  
 Thomas, R. M. See F. J. Moore.  
 Thomas, V., and V. Couderc,  
 i, 401.  
 Torrance, D. M., and N. Knight,  
 ii, 299.

# INDEX OF AUTHORS' NAMES.

y

Treadwell, W. D., ii, 288.  
 Treub, J. P., ii, 303.  
 Tschugaev, L., ii, 322, 335.

## U.

Uhlmann, F., i, 419.

## V.

Valeur, A., i, 403.  
 Venable, C. S., i, 409.  
 Vibrans, F. C. See W. J. Hale.  
 Villiers, A., ii, 332, 333.  
 Villiers, A., and (Mlle.) A. Moreau-Talon, ii, 331.  
 Vorländer, D., ii, 301.  
 Votoček, E., ii, 330.

## W.

Wavre, B. See O. Billater.  
 Wegscheider, R., ii, 298, 304.  
 Weinhagen, A., i, 395.  
 Weiser, H. B., ii, 283.  
 Weiss, P., ii, 291.  
 Wells, H. L., and H. W. Foote, ii, 307.  
 Wereide, T., ii, 288.  
 Werner, A., i, 375.  
 Werner, A., and P. Karrer, ii, 318.  
 Werner, A., and S. Matissen, i, 379.  
 Werner, E. A., i, 380.  
 Werner, E. A., and G. K. Carpenter, TRANS., 694.

Westgren, A., and J. Reitstötter, ii, 301.  
 Wherry, E. T., and E. Yanovsky, ii, 339.  
 White, E. C., and S. F. Acree, ii, 328.  
 White, G. N., i, 387.  
 Widman, O., i, 393.  
 Wiessmann, H., ii, 322.  
 Willstätter, R., and D. Jaquet, i, 391.  
 Willstätter, R., and G. Schudel, i, 399; ii, 337.  
 Windaus, A., ii, 336.  
 Windaus, A., and E. Rahlén, i, 388.  
 Winterstein, H. See E. Hirschberg.  
 Witt, J. C., ii, 321.  
 Wöber, A., ii, 339.  
 Woker, G. See H. Maggi.  
 Wolfrum, L., and J. Pinnow, i, 372.  
 Worrall, D. E., i, 409.

## Y.

Yamazaki, E., i, 414.  
 Yanovsky, E., See E. T. Wherry.

## Z.

Zinke, T., and K. Eismayer, i, 385.  
 Zinke, A., and H. Lieb, i, 398.  
 Zsigmondy, R., and W. Bachmann, ii, 307.

# ERRATUM.

VOL. 114 (ABSTR., 1918).

Page Line  
 i, 343 25 for "benzoyl" read "benzyl."





## CONTENTS

### PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

	PAGE
LXV.—A Study of some Derivatives of Berberine Closely Allied to Derivatives of Cryptopine. By WILLIAM HENRY PERKIN, jun. . . . .	722
LXVI.—Morindone. By JOHN LIONEL SIMONSEN . . . . .	766
LXVII.—The Nitration of 2- and 6-Methoxy- <i>m</i> -tolnaldehydes and <i>m</i> -Toluic Acids. By JOHN LIONEL SIMONSEN . . . . .	775
LXVIII.—The Bromination of some Derivatives of Veratrole. By JOHN LIONEL SIMONSEN and MADYAR GOPALA RAU . . . . .	782
LXIX.—The Electrical Conductivity of Acids and Bases in Aqueous Solutions. By JNANENDRA CHANDRA GHOSH . . . . .	790
XX.—The Freezing Point Curve of Mixtures of Toluene- <i>o</i> - and - <i>p</i> -sulphonamides. Composition of Mixtures of Toluene- <i>o</i> - and - <i>p</i> -sulphonic Acids. By PHYLLIS VIOLET MCKIE . . . . .	799
XXI.—The Compound $H_2B_4O_6$ and its Salts. By RAMES CHANDRA RAY . . . . .	803
XXII.—The Hydrates and Alcoholate of Calcium Benzoate. By FREDERICK STANBRIDGE . . . . .	808
XXIII.— <i>N</i> -Acyl Derivatives of Carbazole. By MAURICE COPIASAROW . . . . .	816

INDEX OF AUTHORS' NAMES.

IN TRANSACTIONS AND ABSTRACTS.

A.

Adamson, W. A. See W. R. Orndorff.  
Amadori, M., ii, 365, 366.  
Anschütz, R., L. Hodenius, M. Maxim, and C. Zymandl, i, 424.  
Anschütz, R., and E. Molineus, i, 423.  
Ariès, E., ii, 352.  
Auffenberg, E. See K. von Auwers.  
Auwers, K. von, ii, 341, 343.  
Auwers, K. von, and E. Auffenberg, i, 436.

B.

Bailey, J. R., and R. H. Pritchett, i, 468.  
Baker, J. C., and L. L. van Slyke, ii, 380.  
Bang, I., ii, 369.  
Barker, H. H., ii, 371.  
Barker, M. F. See J. J. Fox.  
Baudisch, O., i, 430, 474.  
Baudisch, O. See also F. Klaus.  
Bauer, E. See A. Haller.  
Baumann, L., and T. Ingvaldsen, i, 423, 454.  
Bayliss, W. M., i, 461.  
Benedict, S. R. See J. C. Bock.  
Berman, L., ii, 371.  
Beyerinck, M. W., i, 470.  
Biftz, H., and F. Max, i, 455.  
Binder, O. See W. Hoepfner.  
Biatrzycki, A., and W. Schmutz, i, 452.  
Bock, J. C., and S. R. Benedict, ii, 367.  
Boismann, E., i, 423.  
Boon, A. A., and J. Ogilvie, i, 461.  
Boruttau, ii, 345.  
Braun, J. von, i, 450.  
Brooks, S. C., i, 471.  
Bruck, ii, 358.  
Bruhns, G., ii, 368.  
Brunelli, F. E., ii, 352.  
Butironi, C. See M. Padoa.  
Butyendyk, F. J. J., i, 468.

C.

Cambe, J., and H. Diacono, ii, 368.  
Campbell, C., i, 475.  
Campbell, E. de M., ii, 364.  
Casalino, A. See C. Oddo.  
Chapin, R. M., ii, 361.  
Chapin, W. H., ii, 370.  
Chaudun, (Mlle.) A. See H. Colin.  
Chertkov, I., ii, 380.  
Ciamician, C., and C. Ravenna, i, 473.  
Clark, G. W., i, 463.  
Colin, H., and (Mlle.) A. Chaudun, ii, 357.  
Copisarow, M., TRANS., 316.  
Cox, H. E., ii, 356.  
Cusmano, G., i, 434.  
Cwach, J. See J. Stoklasa.

D.

Davissou, B. S., ii, 370.  
Dawson, H. M., ii, 363.  
Delacre, M., i, 422, 423.  
Dernby, K. G., i, 464.  
Diacono, H. See J. Cambe.  
Diels, O., i, 448.  
Dienert, F., ii, 370.  
Dowell, C. T., and W. G. Friedman, ii, 369.  
Downs, C. R., and C. G. Stupp, ii, 376.  
Dubrisay, R., ii, 368.  
Dulk, B. See G. Grube.  
Dupré, F., ii, 376.

E.

Eck, P. N. van, ii, 370.  
Edlbacher, S. See A. Kossel.  
Emery, W. O., and G. C. Spencer, ii, 380.  
Emery, W. O., and C. D. Wright, ii, 378.

F.

Fenner, G., ii, 372.  
Ferguson, J. B., and H. E. Merwin, ii, 362.

Field, A. J., ii, 377.  
 Finzi, C., and E. Vecchi, i, 447.  
 Fiske, C. H., ii, 358.  
 Fox, J. J., and M. F. Barker,  
 i, 427; ii, 374.  
 Franceschi, G., ii, 365.  
 Franzen, H., i, 456.  
 Franzen, H., and C. Mondlange,  
 i, 458.  
 Friedeman, W. G. See C. T.  
 Dowell.

G.

Ganassini, D., ii, 374.  
 Gaubert, P., ii, 355.  
 Gedroitz, K. K., ii, 370.  
 Georgeacopol, E. See A. Schaar-  
 schmidt.  
 Gerhardt, M. See O. Wallach.  
 Ghosh, J. C., TRANS. 790; ii, 348.  
 Gill, A. H., i, 476.  
 Givens, M. H., i, 463.  
 Gonnermann, M., i, 465.  
 Gooch, F. A., and W. Scott, ii, 373.  
 Goto, M., ii, 365.  
 Gradenwitz, H., ii, 367.  
 Grist, W. R. See G. T. Morgan.  
 Groll, J. T., i, 460.  
 Grossfeld, J., ii, 366.  
 Grote, E. See O. Wallach.  
 Grube, G., and B. Dulk, ii, 348.  
 Guinchant, J., i, 422.

H.

Haar, A. W. vander, ii, 376.  
 Haaren, A. van. See E. Hene.  
 Haas, A. R. C., i, 470.  
 Haas, A. R. C. See also W. J. V.  
 Osterhout.  
 Härtel, F., ii, 359.  
 Hahn, O., and L. Meitner, ii, 345.  
 Haller, A., and E. Bauer, i, 428.  
 Hallstein, A. See O. Wallach.  
 Hammarsten, O., i, 459, 460.  
 Hamonet, J., i, 421.  
 Harpater, W. C. See F. M. Seibert.  
 Hart, E. B., G. C. Humphrey, and  
 D. W. Smith, i, 465.  
 Hart, E. B. See also H. H. Som-  
 mer.  
 Hartmann, W. See C. Paal.  
 Harwood, H. E. See P. Jannasch.  
 Haworth, W. N. See J. C. Irvine.  
 Heinrich, G., i, 467.  
 Hemssalech, G. A., ii, 341.  
 Hene, E., and A. van Haaren,  
 ii, 379.  
 Herzenberg, J. See A. Schaar-  
 schmidt.

Herzfeld, E., and R. Klinger,  
 ii, 355.  
 Hiltner, R. S. See C. E. Parker.  
 Hedenius, L. See R. Anschütz.  
 Hoepfner, W., and O. Binder,  
 ii, 372.  
 Horák, O. See J. Stoklassa.  
 Humphrey, G. C. See E. R. Hart.

I.

Ingvaldsen, T. See L. Baumann.  
 Irvine, J. C., and W. N. Haworth,  
 i, 421.  
 Issakutz, B. von, i, 462, 467.  
 Issoglio, G., i, 476.

J.

Jacoby, M., i, 469.  
 Jannasch, P., and H. E. Harwood,  
 ii, 373.  
 Jenni, E., i, 462.  
 Jessen, W. See O. Wallach.  
 Jodidi, S. L., ii, 379.  
 Johlin, J. M., ii, 358.  
 Jong, A. W. K. de, i, 432.  
 Justin-Mueller, E., ii, 360.

K.

Kalcher, K., i, 433.  
 Karaoglanow, Z., ii, 369.  
 Kawase, S., i, 476.  
 Kehrman, F., i, 449.  
 Kehrman, F., and M. Sandoz,  
 ii, 344.  
 Kiplinger, C. C., ii, 360.  
 Klaus, F., and O. Baudisch, i, 430.  
 Kligler, J., i, 468.  
 Klinger, R. See E. Herzfeld.  
 Kober, P. A., ii, 359.  
 Kolthoff, I. M., ii, 377.  
 Komatsu, S., i, 426.  
 Komppa, G., and R. H. Roschier,  
 i, 429, 445.  
 Korten, E. See A. Schaar-  
 schmidt.  
 Kossel, A., and S. Edlbacher,  
 i, 463.  
 Kotake, Y., and Z. Matsuoaka,  
 i, 467.  
 Kylin, H., i, 476.

L.

Lagerlöf, D., ii, 353.  
 La Rosa, M., ii, 362.  
 Leclère, A., ii, 369.

Leeuwen, W. S. van, i, 463.  
 Lenci, F., ii, 360.  
 Levene, P. A., and F. A. Taylor,  
 i, 422.  
 Levene, P. A., and C. J. West,  
 i, 421.  
 Lichtenstadt, L. See L. Semper.  
 Lo Monaco, D., i, 466.  
 Lüders, H. See R. Meyer.  
 Lynas, W. H., ii, 365.

## M.

McKie (Miss) P. V., TRANS., 799.  
 Masing, G., ii, 354.  
 Matsuo, I., 466.  
 Matsuo, Z., i, 467.  
 Matsuo, Z. See also Y. Kotake.  
 Mauthner, F., i, 428.  
 Max, F. See H. Biltz.  
 Maxim, M. See R. Anschütz.  
 Meitner, L., ii, 347.  
 Meitner, L. See also O. Hahn.  
 Menke, J. B., ii, 371.  
 Merwin, H. E. See J. B. Ferguson.  
 Meyer, R., and H. Lüders, i, 450.  
 Meyerhof, O., i, 464.  
 Milbauer, J., ii, 360.  
 Molineus, E. See R. Anschütz.  
 Moller, L., i, 469.  
 Mondlange, C. See H. Franzen.  
 Morgan, G. T., and W. R. Grist,  
 i, 450.  
 Mori, Y., i, 466.  
 Munn, W. F., ii, 375.

## N.

Némec, A. See J. Stoklasa.  
 Neuberg, C., i, 423, 469.  
 Nomura, H., i, 446.  
 Nomura, H., and F. Nozawa,  
 i, 438.  
 Northrup, Z., i, 463.  
 Nozawa, F. See H. Nomura.

## O.

Oddo, G., ii, 352.  
 Oddo, G., and A. Casalino, ii, 352.  
 Ogilvie, J. See A. A. Boon.  
 Orndorff, W. R., and W. A. Adamson, i, 435.  
 Osterhout, W. J. V., i, 462, 470,  
 471, 472.  
 Osterhout, W. J. V., and A. R. C.  
 Haas, i, 470.

Ostwald, W., ii, 367.  
 Oyen, L. W. H. van, i, 472.

## P.

Paal, C., and W. Hartmann, ii, 357.  
 Pados, M., and C. Butironi, ii, 345.  
 Palkin, S., ii, 375.  
 Parker, C. E., and R. S. Hiltner,  
 ii, 377.  
 Payman, W., and R. V. Wheeler,  
 ii, 356.  
 Pelikan, K. See O. Wallach.  
 Perkin, W. H. jun., TRANS., 722.  
 Piccard, J., and M. Rising, i, 466.  
 Poch, P., ii, 373.  
 Pollecoff, (Miss) F., and R. Robin-  
 son, i, 427.  
 Ponte, G., ii, 366.  
 Pritchett, R. H. See J. R. Bailey.

## R.

Randall, W. W., ii, 367.  
 Rau, M. G. See J. L. Simonsen.  
 Ravenna, C. See G. Ciamician.  
 Ray, R. C., TRANS., 803.  
 Rechenberg, W. von. See O.  
 Wallach.  
 Reverdin, F. A. Rilliet, and C.  
 Vernet, i, 455.  
 Rhead, T. F. E., ii, 362.  
 Rilliet, A. See F. Reverdin.  
 Ringer, W. E., i, 459.  
 Rising, M. See J. Piccard.  
 Rittenhouse, E., ii, 358.  
 Robinson, (Mrs.) G. M., and R.  
 Robinson, i, 448.  
 Robinson, R. See (Miss) F. Polle-  
 coff, and (Mrs.) G. M. Robinson.  
 Roschier, R. H. See G. Komppa.  
 Rupp, E., ii, 369.

## S.

Sandoz, M. See F. Kehrman.  
 Schaarschmidt, A., and E.  
 Georgeacopol, i, 434.  
 Schaarschmidt, A., E. George-  
 acopol, and J. Herzenberg, i, 431.  
 Schaarschmidt, A., and E. Kor-  
 ten, i, 433.  
 Schenck, R., ii, 355.  
 Schmutz, W. See A. Bistrzycki.  
 Schorlemmer, K., ii, 372.  
 Scott, W. See F. A. Gooch.  
 Sebor, J. See J. Stoklasa.  
 Seibert, F. M., and W. C. Harp-  
 ster, ii, 367.

# INDEX OF AUTHORS' NAMES.

Semper, L., and L. Lichtenstadt, i, 437.  
 Sernagiotto, E., i, 444.  
 Serra, A., ii, 348.  
 Silberstein, F., i, 464.  
 Simonsen, J. L., TRANS., 766, 775.  
 Simonsen, J. L., and M. G. Rau, TRANS., 782.  
 Slyke, L. L. Van. See J. C. Baker.  
 Smith, D. W. See E. B. Hart.  
 Société Chimique des Usines du Rhône, i, 422.  
 Society of Chemical Industry in Basle, i, 450.  
 Somieski, C. See A. Stock.  
 Sommer, H. H., and E. B. Hart, i, 465.  
 Spencer, G. C. See W. O. Emery.  
 Stanbridge, F., TRANS., 808.  
 Standacher, M. See O. Wallach.  
 Steenbock, H., i, 476.  
 Stock, A., ii, 353.  
 Stock, A., and C. Somieski, ii, 361.  
 Stoklasa, J., J. Cwach, O. Horák, A. Némec, J. Sebor, F. Týmich, and W. Zdobnický, i, 475.  
 Stupp, C. G. See C. R. Downs.

## T.

Taney, H. F., ii, 372.  
 Taylor, F. A. See P. A. Levene.  
 Thuras, A. L. See E. E. Weibel.  
 Tillisch, H., ii, 368.  
 Týmich, F. See J. Stoklasa.

## V.

Vacchi, E. See C. Finzi.  
 Vernet, C. See F. Reverdin.  
 Värtheim, A., ii, 371.

## W.

Waard, D. J. de, ii, 359.  
 Wallach, O., M. Gerhardt, and W. Jessen, i, 442.  
 Wallach, O., E. Grote, A. Hallstein, W. Jessen, H. E. Woodman, i, 440.  
 Wallach, O., and K. Pelikan, i, 445.  
 Wallach, O., and W. von Rechenberg, i, 428.  
 Wallach, O., and M. Standacher, i, 444.  
 Wallach, O., M. Walter, and J. Wolff, i, 440.  
 Walter, M. See O. Wallach.  
 Weber, F. C., and J. B. Wilson, ii, 377.  
 Wegscheider, R., ii, 349.  
 Weibel, E. E., and A. L. Thuras, ii, 368.  
 Weigert, F., ii, 344.  
 Weiss, F. L., ii, 374.  
 Weiss, P., ii, 354.  
 West, C. J. See P. A. Levene.  
 Wheeler, R. V. See W. Payman.  
 Wilson, J. B. See F. C. Weher.  
 Wilson, L. A., ii, 371.  
 Winter, O. B., ii, 364.  
 Wislicenus, H., i, 472.  
 Witzemann, E. J., i, 422.  
 Wolf, K., ii, 350.  
 Wolff, J. See O. Wallach.  
 Woodman, H. E. See O. Wallach.  
 Wright, C. D. See W. O. Emery.

## Z.

Zdobnický, W. See J. Stoklasa.  
 Zeehuisen, H. See H. Zwaardemaker.  
 Zwaardemaker, H., and H. Zeehuisen, ii, 351.  
 Zymandl, C. See R. Anschütz.

# ERRATA.

VOL. 114 (ABSTR., 1918).

Page	Line	
i, 342	15*	for " <i>p</i> -Aminophenol" read " <i>p</i> -Nitrophenol."
ii, 323	10	for "Sulpharsenate" read "Sulpharsenite."
	15	for "5%" read "25%."
ii, 326	12*	for "Vasca" read "Vaca."

\* From bottom



## CONTENTS

### PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

	PAGE
LXXIV.—The Relative Activity of certain Alkyl Iodides with Sodium $\alpha$ -Naphthoxide in Methyl Alcohol. By HENRY EDWARD COX . . . . .	821
LXXV.—The Hydrolysis of Soap Solutions, Measured by the Rate of Catalysis of Nitrosotriacetoneamine. By JAMES WILLIAM MCBAIN and THOMAS ROBERT BOLAM . . . . .	825
LXXVI.—Studies in the Phenylsuccinic Acid Series. Part VII. The Action of Alcohols and Amines on $\gamma$ -Diphenylsuccinic Anhydride. By HENRY WREN and HOWELL WILLIAMS . . . . .	832
LXXVII.—The Inflammation of Mixtures of Methane and Air in a Closed Vessel. By RICHARD VERNON WHEELER . . . . .	840
LXXVIII.—A Synthesis of <i>iso</i> Brazilein and certain Related Anhydropyranol Salts. Part I. By HERBERT GRACE CRABTREE, ROBERT ROBINSON and MAURICE RUSSELL TURNER . . . . .	859
LXXIX.—The Action of Chlorine on the Alkali Iodides. By WILLIAM NORMAN RAE . . . . .	880
LXXX.—Hydroxylamine Platinum Bases. By LEO ALEXANDROWITSCH TSCHUGAEV and ILJA ILWITSCH TSCHERNJAEV . . . . .	884
LXXXI.—Trimorphic Change of 4-Nitroaceto- <i>o</i> -toluidide. By FREDERICK DANIEL CHATTAWAY . . . . .	897
LXXXII.—The Preparation of Ethylamine and of Diethylamine. By EMIL ALPHONSE WERNER. . . . .	899



# INDEX OF AUTHORS' NAMES.

## IN TRANSACTIONS AND ABSTRACTS.

### A.

Adams, R., and O. Kamm, i, 842.  
Adler, J. See R. Scholl.  
Auffenberg, E. See K. von Auwers.  
Auwers, K. von, ii, 381.  
Auwers, K. von, and E. Auffenberg, i, 479.

### B.

Bado, A. A., ii, 402.  
Balareff, D., ii, 406.  
Barnett, G. D., and H. S. Chapman, ii, 404.  
Bau, A., ii, 412.  
Baudisch, O., i, 496; ii, 412.  
Bauer, E., F. Weiss, and A. Piccard, ii, 387.  
Bechhold, H., i, 516.  
Bell, H., ii, 393.  
Berczeller, L., ii, 390.  
Berger, H. See A. Darapsky.  
Bernthsen, W., i, 486.  
Berthoud, A., ii, 388.  
Bertiaux, L., ii, 408.  
Bertsch, E. See R. Scholl.  
Berwerth, F., ii, 403.  
Bierry, H., and (Mme.) L. Randoine-Vanard, ii, 416.  
Binder, O., ii, 398.  
Blükenhorn, H. See F. Straus.  
Blount, B., ii, 396.  
Bolam, T. R. See J. W. McBain.  
Bougault, ii, 413.  
Boutwell, P. W. See H. Steenbock.  
Bouvet, M., ii, 397.  
Brandt, L., ii, 409.  
Brann, A., ii, 393, 394.  
Brieger, W., ii, 396.  
Bunschoten, E., i, 503.

### C.

Caesar, E., i, 512.  
Chapman, H. S. See G. D. Barnett.

Chattaway, F. D., TRANS., 897.  
Chemische Fabrik von Heyden, i, 482.  
Collie, J. N., and H. E. Watson, ii, 383.  
Coudere, V. See V. Thomas.  
Cox, H. E., TRANS., 821.  
Crabtree, H. G., R. Robinson, and M. R. Turner, TRANS., 859.  
Crawford, D. See J. E. Saul.  
Crozier, W. J., i, 514.

### D.

Darapsky, A., H. Berger, and M. Prabhakar, i, 506.  
Davis, H. S., and M. D. Davis, ii, 410, 411.  
Davis, H. S., M. D. Davis, and D. G. MacGregor, ii, 411.  
Davis, M. D. See H. S. Davis.  
Denis, W., ii, 414.  
Dorfmueller, G. See S. J. Thannhauser.  
Dunncliff, H. B., and S. Lal, ii, 398.

### E.

Eckert, A. See H. Meyer.  
Egerer, G., i, 496.  
Eigenberger, F., i, 512.  
Elsdon, G. D., ii, 412.  
Ernst, T. R., ii, 396.  
Euler, H., and O. Svanberg, i, 511.

### F.

Farbenfabriken vorm. F. Bayer & Co., i, 494.  
Feigl, J., i, 514.  
Fellenberg, T. von, ii, 415.  
Fiedler, L. v. See J. Pollak.  
Foch, T. See O. Ruif.  
Fouchet, A., ii, 415.  
Freundlich, H., and J. Reikstötter, ii, 393.

G.

Gaarder, T., i, 512.  
Gaubert, P., ii, 393.  
Gaza, W. von, i, 514.  
Gedroitz, K. K., i, 519, 520.  
Ghosh, J. C., ii, 392.  
Goerens, F. See E. Ruer.  
Goeh, F. A., and M. A. Soderman,  
ii, 408.  
Gortner, R. A., ii, 416.  
Graaff, W. C. de, i, 510.  
Greenwald, L., i, 513.  
Grüttner, G., and E. Krause, ii, 382.  
Gutmann, S., ii, 409.

H.

Haack, I. W. D., ii, 396.  
Hammarsten, O., i, 509, 510.  
Hardtke, O., ii, 385.  
Harned, H. S., and C. N. Laird,  
ii, 412.  
Heinisch, W., ii, 413.  
Hemsalech, G. A., ii, 384.  
Herz, W., ii, 389.  
Herzfeld, E., and R. Klinger,  
ii, 415.  
Herzig, J., K. Landsteiner, M.  
Quittner, and F. Zippner, i, 508.  
Herzig, J., and H. Lieb, i, 504.  
Herzig, J., and G. Tiring, i, 503.  
Hitch, A. R., ii, 398.  
Holmes, H. N., ii, 392.  
Hopkins, B. S. See L. F. Yntema.  
Howden, R., ii, 408.

I.

Iles, L. E., ii, 407.

J.

Jacoby, M., i, 517.  
Johnson, A. J. See H. E. Patten.  
Jones, E. G., ii, 410.  
Jones, L. W., and L. Werner,  
i, 483.

K.

Kamm, O. See R. Adams.  
Kaleman, G., i, 511.  
Kent, H. E. See H. Steenbock.  
Kleinschmidt, A., ii, 400.  
Klinger, R. See E. Herzfeld.  
Klingler, A. See R. Weitzen-  
bock.

Kögel, P. R., i, 515.  
Koenig, J. See P. Nicolardot.  
Koenigsberger, J. See W. J.  
Müller.  
Koessler, J. H., i, 519.  
Kohlrausch, K. W. F., ii, 386.  
Kohn, M., and V. Neustädter,  
i, 477.  
Kohn, M., and A. Ostertsetzer,  
i, 501.  
Krause, E. See G. Grüttner.  
Kubelka, V., ii, 390.

L.

Laird, C. N. See H. S. Harned.  
Lal, P. See N. C. Nag.  
Lal, S. See H. B. Dunncliff.  
Landaburu, J. L. See E. V. Zappi.  
Landsteiner, K. See J. Herzig.  
Langhans, A., ii, 414.  
Lenko, J. See R. Scholl.  
Leone, R., ii, 416.  
Lewis, J. H., i, 513.  
Lieb, H., and A. Zinke, i, 502.  
Lieb, H. See also J. Herzig.  
Lilienfeld, J. E., and H. Seemann,  
ii, 383.  
Loeb, J., i, 510.  
Loring, F. H., ii, 396.  
Lucas, R., ii, 391.

M.

McBain, J. W., and T. R. Bolam,  
TRANS., 825.  
MacGregor, D. G. See H. S. Davis.  
Macht, D. L., i, 515.  
Mains, G. H. See H. E. Patten.  
Marini, C., i, 518.  
Masling, G., ii, 389.  
Masson, G., i, 518.  
Merck, K. See J. Thiele.  
Meyer, H., and A. Eckert, ii, 385.  
Milobendzki, T., and A. Sach-  
nowski, i, 477, 478.  
Milobendzki, T., and K. Szulgin,  
i, 495.  
Milobendzki, T., and M. Szwej-  
kowska, i, 479.  
Moeller, W., ii, 392.  
Müller, W. J., and J. Koenigs-  
berger, ii, 402.  
Mummery, W. R., ii, 406.

N.

Nag, N. C., and P. Lal, ii, 411.  
Nagai, N., i, 500.  
Nakaseko, R., ii, 416.

Neuberg, C., and E. Reinfurth, i, 517.  
 Neuberger, W. See R. Scholl.  
 Neustädter, V. See M. Kohn.  
 Newbery, E., ii, 387.  
 Nicolardot, P., and J. Koenig, ii, 407.

## O.

Oelsner, A., ii, 405.  
 Ostersetzer, A. See M. Kohn.  
 Ostwald, W., ii, 391.  
 Osugi, S. See F. E. Rice.  
 Oxley, A. E., ii, 387.

## P.

Patten, H. E., A. J. Johnson, and G. H. Maina, ii, 387.  
 Peltriset, C. N., ii, 414.  
 Pépin, G., ii, 414, 415.  
 Piccard, A. See E. Bauer.  
 Pinnow, J., ii, 394.  
 Pohl, J., i, 515.  
 Pollak, J., L. v. Fiedler, and H. Roth, i, 498.  
 Pollak, J., and B. Schadler, i, 497.  
 Polonovski, Max, i, 505.  
 Polonovski, Max, and Michel Polonovski, i, 504.  
 Polonovski, Michel. See Max Polonovski.  
 Powell, A. R., ii, 410.  
 Prabhakar, M. See A. Darapsky.

## Q.

Quittner, M. See J. Herzog.

## R.

Radsma, W., i, 511.  
 Rae, W. N., TRANS., 880.  
 Randoin-Vanard (Mme.) L. See H. Bierry.  
 Rappleye, W. C., ii, 404.  
 Reinfurth, E. See C. Neuberg.  
 Reitschötter, J. See H. Freundlich.  
 Renaud, A., ii, 405, 407.  
 Reutter, L., i, 496.  
 Rice, F. E., and S. Osugi, i, 520.  
 Robinson, R. See H. G. Crabtree.  
 Rodebush, W. H., ii, 388.  
 Röhling, H. See E. H. Zollinger.  
 Roth, H. See J. Pollak.

Ruer, R., and F. Goerens, ii, 399.  
 Ruff, O., and T. Foehr, ii, 399.

## S.

Sachnowski, A. See T. Milobendzki.  
 Salkowski, E., i, 514.  
 Sato, A., ii, 406.  
 Saul, J. E., and D. Crawford, ii, 408.  
 Schadler, B. See J. Pollak.  
 Scheringa, K., ii, 409.  
 Schmidt, G. C., ii, 386.  
 Scholl, R., and J. Adler, i, 482.  
 Scholl, R., and E. Bertsch, i, 495.  
 Scholl, R., and J. Lenko, i, 484, 506.  
 Scholl, R., and W. Neuberger, i, 505.  
 Scholl, R., W. Neuberger, and W. Tritsch, i, 484.  
 Seemann, H. See J. E. Lilienfeld.  
 Sławiński, K., i, 481, 502.  
 Smith, Alpheus W., and Alva W. Smith, ii, 388.  
 Smith, Alva W. See Alpheus W. Smith.  
 Society of Chemical Industry in Basle, i, 496.  
 Soderman, M. A. See F. A. Gooch.  
 Stang-Lund, F. See L. Wöhler.  
 Steel, T., ii, 407.  
 Steenbock, H., P. W. Boutwell and H. E. Kent, i, 513.  
 Stewart, A. W., ii, 395.  
 Straus, F., and H. Blankenhorn, i, 501.  
 Svanberg, O. See H. Euler.  
 Szperl, L., i, 492.  
 Szperl, L., and T. Wierusz-Kowalski, i, 492.  
 Szulgin, K. See T. Milobendzki.  
 Szwejkowska, M. See T. Milobendzki.

## T.

Thannhauser, S. J., and G. Dorf-müller, i, 513.  
 Thiele, J., and K. Merck, i, 484.  
 Thomas, V., and V. Coudert, i, 504.  
 Tiring, G. See J. Herzog.  
 Tribondeau, L., ii, 416.  
 Tritsch, W. See R. Scholl.  
 Tschernjaev, I. I. See L. I. Tschugaev.  
 Tschugaev, L. A., and I. I. Tschernjaev, TRANS., 884.  
 Turner, M. R. See H. G. Crabtree.

# INDEX OF AUTHORS' NAMES.

## U.

Unger, R., i, 515.

## V.

Vermande, J., ii, 397.

## W.

Waddell, J., ii, 407.

Waser, E., i, 515.

Waterman, H. L., i, 518; ii, 404.

Watson, H. E. See J. N. Collie.

Weevers, T., i, 518.

Wegscheider, R., ii, 394.

Weiss, P. See E. Bauer.

Weitzenböck, R., i, 493.

Weitzenböck, R., and A. Klingler, i, 494.

Werner, E. A., TRANS., 899.

Verner, L. See L. W. Jones.

Wheeler, R. V., TRANS., 840.

Vierusz-Kowalski, T. See L. Szperl.

Williams, H. See H. Wren.

Windaus, A., i, 500.

Winderlich, R., ii, 409.

Wöhler, L., and F. Stang-Lund, ii, 397.

Wolter, L., ii, 414.

Wren, H., and H. Williams, TRANS., 832.

Wüest, H. M., i, 488.

## Y.

Yamada, M., i, 511.

Yntema, L. F., and B. S. Hopkins, ii, 398.

## Z.

Zappi, E. V., i, 483.

Zappi, E. V., and L. J. Landaburu, i, 510; ii, 398.

Zinke, A. See H. Lieb.

Zipperer, F. See J. Herzig.

Zollinger, E. H., and H. Röhling, i, 497.

Zotier, V., ii, 403.



aqueous alkalis, but dissolving in alcohol to a magenta solution. It separated from this solution in ill-defined crystals, which, after washing with ether, melted at 160—161°:

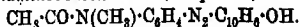
0.1426 gave 17.3 c.c.  $N_2$  at 25° and 763 mm.  $N = 13.81$ .

$C_{18}H_{15}O_2N_3$  requires  $N = 13.76$  per cent.

*p*-Aminomethylformanilide was diazotised and combined with the following phenolic substances: salicylic acid,  $\alpha$ -naphthol-4-sulphonic acid (N and W acid), and 8-amino- $\alpha$ -naphthol-3:6-disulphonic acid (H acid), giving rise to a series of azo-dyes, the properties of which are tabulated below.

*Azo-derivatives of p-Aminomethylacylanilides.*

Base.	Phenolic compound.	Colour.	Azo-dye.		Colour with concentrated sulphuric acid.
			Dyeing effect on wool (a) and silk (b).		
<i>p</i> -Amino-methyl-form-anilide.	Salicylic acid	orange-brown powder.	a. brownish-yellow	b. lemon-yellow	orange-brown
	$\beta$ -Naphthol	ill-defined dark red nodules			crimson
	"N & W" acid	dark red powder	russet brown	brownish-red	reddish-brown.
	"H" acid	deep purple powder	brownish-purple	"royal" purple	dark brownish-red, crimson on dilution.
<i>p</i> -Amino-methyl-acet-anilide.	Salicylic acid	brownish-yellow powder	greenish-yellow	golden-yellow	bright orange-brown
	$\beta$ -Naphthol	well-defined red needles			bright crimson
	"N & W" acid	orange-red powder	scarlet	scarlet	reddish-brown
	"H" acid	purple powder	bluish-purple reddened by meta-chrome mordant	"Bordeaux" red	crimson

*Acetylmethylaminobenzene-4-azo-β-naphthol,*

—This azo-derivative was obtained by grinding together acetylmethylaminobenzene-4-diazo-hydroxide and β-naphthol; the mixture rapidly turned red and became moist owing to the elimination of water due to the azo-condensation. It was also prepared by diazotising *p*-aminomethylacetanilide in cold concentrated hydrochloric acid, the solution of the soluble diazonium chloride being added to alkaline β-naphthol. The product crystallised from alcohol in well-defined, transparent, red tablets or flattened needles melting at 139°:

0.1414 gave 16.1 c.c.  $\text{N}_2$  at 17° and 766 mm.  $\text{N}=13.34$ .

$\text{C}_{20}\text{H}_{17}\text{O}_2\text{N}_3$  requires  $\text{N}=13.15$  per cent.

*p*-Aminomethylacetanilide was also combined with several other phenolic substances, giving rise to the above azo-dyes.

The authors desire to express their thanks to Mr. A. W. B. Upton, A.C.G.F.C., for assistance in the preliminary experiment of this investigation.

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LX.—*The Constitution of Carbamides. Part VII.*  
*The Mechanism of the Synthesis of Urea from the*  
*Interaction of Carbonyl Chloride and Ammonia.*  
*Part VIII. The Formation of Urea and of*  
*Biuret from Oxamide*

By EMIL ALPHONSE WERNER and (Part VIII.) GEORGE KINGSFORD  
CARPENTER.

THE formation of urea from the interaction of carbonyl chloride and ammonia has been generally considered to be a direct change analogous, for example, to the formation of acetamide from the interaction of acetyl chloride and ammonia. For this reason, this synthesis of urea is invariably set forth as 'conclusive' evidence of the 'carbamide' formula. This is mainly due to the fact that the so-called secondary products have been ignored, so far as their bearing on the mechanism of the change is concerned. Given the consideration they deserve, they clearly indicate the true origin of

urea in this reaction, which in truth is no more than Wöhler's synthesis in another form.

Natanson (*Annalen*, 1856, **98**, 287) first isolated urea from this reaction, Regnault (*Ann. Chim. Phys.*, 1838, [ii], **69**, 180) having obtained indications of its formation.

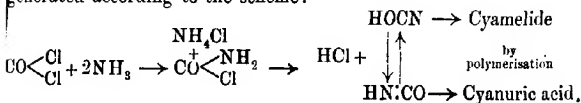
Bouchardat (*Compt. rend.*, 1869, **69**, 961) showed that cyanuric acid and ammeline were formed in addition to urea; Fenton (T., 1879, **35**, 793) suggested that urea was possibly the result of a secondary reaction, on account of the small proportion obtained. Hantzsch and Stuer (*Ber.*, 1905, **38**, 1041, 2326) found cyamelide as an additional product when ammonia was passed into a solution of carbonyl chloride in light petroleum at 0°. This fact is of interest, since it confirms the author's theory of the constitution and polymerisation of cyanic acid (T., 1913, **103**, 1017).

*Origin of Urea, and Formation of Biuret in the Interaction of Carbonyl Chloride and Ammonia.*

If urea had the 'carbamide' structure, there appears no reason why it should not be formed in quantitative yield without the accompaniment of several secondary products. In view of the evidence, it is remarkable that no explanation of this has yet been suggested.

The cause undoubtedly lies in the recognition of the fact that there exists no tendency to the formation of a compound containing the system  $\text{C}(\text{NH}_2)_2$ , since this cannot form a part of a stable molecule (this vol., p. 624).

It is evident that the formation of cyanuric acid and of cyamelide arises from the polymerisation of cyanic acid ( $\text{HO-CN} \rightleftharpoons \text{HN}:\text{CO}$ ), generated according to the scheme:



Cyanic acid being generated in the presence of ammonia, the origin of urea in this synthesis is self-evident. In support of this explanation of the change, it was found that biuret constituted large part of the secondary products, since it was shown (T., 1913, **103**, 1014, 2278; P., 1914, **30**, 262) that whilst biuret is formed from the union of cyanic acid and urea, ammeline is formed from the interaction of cyanic acid and biuret. It is not surprising that the formation of the latter has been overlooked by previous investigators, since there was no reason to expect its production according to the usual, but incorrect, view of the change.



In order to place on record information as regards the relative proportions of the different products formed, a quantitative study of the reaction at different temperatures has been made.

The following results were obtained after passing a current of dry ammonia into a 3 per cent. solution of carbonyl chloride in benzene until decomposition was completed :

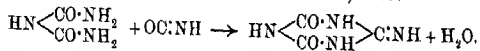
	Expt. I.	Expt. II.	Expt. III.
Temperature .....	20—25°	40—50°	65—70°
Products formed .....	Per cent.	Per cent.	Per cent.
Urea .....	31.7	37.3	41.2
Biuret .....	14.4	10.1	7.8
Ammelide .....	7.65	8.6	10.6
Cyanuric acid .....	3.45	6.4	5.98.
Cyameliide .....	0.69	trace	none

The results are expressed in proportion to the respective theoretical yields, calculated on the following bases: thus  $\text{COCl}_2 = \text{one mol.}$  each of urea, cyanuric acid, and cyamelide, since the two latter are formed from the polymerisation of cyanic acid,  $2\text{COCl}_2 = \text{one mol.}$  of biuret, and  $3\text{COCl}_2 = \text{one mol.}$  of ammelide.

It will be noticed that in Expts. I and II biuret constitutes the chief product after urea, and whilst the yield falls with rise of temperature, that of ammelide increases, since, in agreement with theory (*loc. cit.*), the formation of the latter from its precursor biuret is promoted at the higher temperature. The condition being unfavourable for the existence of free cyanic acid, the proportion of cyanuric acid generated was consequently small.

After the crude product from Expt. I had been shaken with a small quantity of pure alcohol, ethyl allophanate ( $\approx 5.3$  per cent of the theoretical) was extracted from the benzene-alcohol filtrate. This could only have resulted from a reaction with cyanic acid generated from the substance,  $\text{NH}_2\cdot\text{COCl}$ , present in the original product, thus,  $2\text{NH}_2\cdot\text{COCl} + \text{C}_2\text{H}_5\cdot\text{OH} = \text{C}_4\text{H}_5\text{O}_3\text{N}_3 + 2\text{HCl}$ .

Whilst the total chlorine content of the carbonyl chloride was accounted for as ammonium chloride and a small quantity of chloroformamide, it will be seen, from the sum of the other products taking an average for the three experiments, that only about 65 per cent. of the carbonyl group was recovered. The deficiency was due to decomposition of carbonyl chloride by water generated simultaneously with the formation of ammelide, thus:



When ammonia dissolved in benzene was added to an excess of carbonyl chloride in the same solvent (ratio,  $\text{COCl}_2 + 2\text{NH}_3$ ), the yield of urea was equal to only 4.6 per cent. of the theoretical. Cyamelide and cyanuric acid were formed in appreciable amount;

biuret and ammelide were absent. Whilst much carbonyl chloride was unchanged, the solution contained 19 per cent. of the theoretical yield of the compound,  $\text{NH}_2\cdot\text{COCl}$  (Expt. IV).

Boucharlat's (*loc. cit.*) conclusion that guanidine was formed in this reaction could not be confirmed.

In support of the author's contention as regards the system  $\text{C}(\text{NH}_2)_2$ , and in confirmation of the present theory of the formation of urea in this reaction, it may be pointed out that thiourea is not formed from the interaction of ammonia and thiocarbonyl chloride. The fact that ammonium thiocyanate is produced instead supplies a convincing argument.

#### EXPERIMENTAL.

The following method was adopted in obtaining the results given under Expts. I, II, and III: 12 grams of carbonyl chloride dissolved in 400 c.c. of freshly distilled benzene were placed in a stout, wide-mouthed bottle provided with a cork which carried a delivery tube, thermometer, and exit tube. A slow current of dry ammonia (generated as described later) was delivered on to the surface of the liquid, which was kept continually agitated. On account of the rather gelatinous form of the product, it was scarcely possible to ensure uniformity in the progress of the reaction or to maintain a constant temperature. In Expt. I, the vessel was immersed in water at  $0^\circ$ , in Expt. II in water at  $15^\circ$ , in Expt. III no artificial cooling was used. The higher temperature given represents the maximum attained during the progress of each experiment.

The details of Expt. I will suffice to illustrate how the different products were estimated.

The solid material, after being washed with benzene, was collected, dried, and extracted with warm alcohol; the residue (2.04 grams of ammonium chloride present), on treatment with water, left 0.436 gram of insoluble matter, from which 0.4 gram of ammelide was extracted by solution in sodium hydroxide. Hence ammelide present = 0.036 gram. The alcoholic extract was concentrated by evaporation to a small volume; 2.25 grams of crystalline matter (A) separated after cooling, and the mother liquor on evaporation to dryness left a residue (B) = 2.45 grams.

Product (A) contained 0.96 gram of ammonium chloride and 0.95 gram of urea; cyanuric acid was absent, and the remainder (0.34 gram) was chiefly ethyl allophanate with a trace of biuret. Product (B) was dissolved in 50 c.c. of water. Cyanuric acid was estimated in an aliquot portion by titration with  $N/10$ -sodium

hydroxide, using phenolphthalein as indicator: required for total 14 c.c.  $N/10$ - $\text{NaOH}$  = 0.18 gram  $\text{C}_3\text{H}_5\text{O}_3\text{N}_3$ .

Biuret was estimated colorimetrically, as previously described (T., 1913, 103, 2282). Found, 0.897 gram; it was also separated in crystalline form and identified (m. p. 192°).

Urea was estimated in this solution by precipitation as nitrate, which was washed with ether, dried, and weighed.

Urea found = 1.36. Hence total urea  $(A) + (B)$  = 2.31 grams = 31.7 per cent. of the theoretical amount from 12 grams of carbonyl chloride.

Since guanidine can be detected with ease, even in a 0.1 per cent. solution and in the presence of urea, and of biuret by means of picric acid, its absence was proved by the negative result obtained with this reagent.

*Expt. IV.—Interaction of Carbonyl Chloride and Two Molecular Proportions of Ammonia.*—To 4 grams of carbonyl chloride in 100 c.c. of benzene, 0.68 gram of ammonia dissolved in 200 c.c. of benzene was added.

The precipitated material was washed with benzene, collected, dried, and extracted with alcohol. The amount of urea found in the resulting solution, after removal of ammonium chloride, was 0.0278 gram = 4.6 per cent. of the theoretical. The benzene filtrate was shaken with a slight excess of pure sodium hydroxide solution, to which, after neutralisation, an excess of silver nitrate was added. The washed precipitate of silver chloride and silver cyanate was digested with dilute nitric acid to remove the latter salt. The resulting solution required, for precipitation of the silver, 76.8 c.c. of  $N/10$ -potassium thiocyanate, equal to 19 per cent. of the theoretical amount of the compound,  $\text{NH}_2\cdot\text{COCl}$ , present in the benzene solution; thus  $\text{NH}_2\cdot\text{COCl} + 2\text{NaOH} = \text{NaOCN} + \text{NaCl} + 2\text{H}_2\text{O}$ .

*Note on a Convenient Method for obtaining a Continuous Current of Dry Ammonia without the Application of Heat.*

The following method has given admirable results, and it seemed worth while to place it on record. It is adaptable to any scale and where, for example, it was required to saturate 8 litres of alcohol with dry ammonia, the procedure was as follows.

Ammonia solution (D 0.880) was allowed to drop from a separating funnel at a regulated rate on 400 grams of commercial sodium hydroxide, in coarse powder, contained in a round-bottomed flask of about 4 litres capacity. The gas was rapidly liberated.

and the temperature of the mixture gradually fell to nearly zero. The process required no attention beyond occasionally replenishing the supply of ammonia solution; nearly 90 per cent. of the ammonia from 1500 c.c. of the concentrated solution was obtained without any application of heat. In order to avoid interference with the continuity of the process through the effects of back pressure, it was necessary to connect the limb of the separating funnel with a short length of glass tubing drawn out to an aperture of about 1.5 mm., whereby the necessary hydrostatic pressure was maintained.

*Summary.*

(1) The synthesis of urea from the interaction of carbonyl chloride and ammonia does not supply evidence in support of the carbamide' formula.

(2) A quantitative study of the interaction, and the nature and number of the secondary products, has shown that urea is produced from the union of ammonia and cyanic acid (in the keto-form), generated from the decomposition of the compound,  $\text{H}_2\text{N}\cdot\text{COCl}$ , produced in the first instance.

(3) It is shown, for the first time, that biuret is a product of his reaction.

*Part VIII.—The Formation of Urea and of Biuret from Oxamide.* [With GEORGE KINGSFORD CARPENTER.]

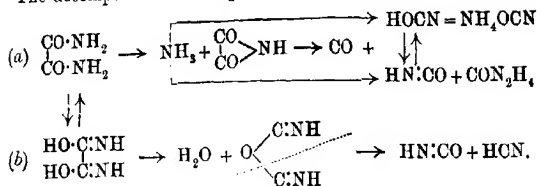
Many years ago, Williamson (*Memoir, Congrès. Scientif. de Venise*, 1847 \*) obtained urea by heating a mixture of oxamide and mercuric oxide. This has been accepted as evidence of a close connexion in constitution between urea and the diamide, the latter being supposed merely to lose a carbonyl group in the change.

An investigation of the mechanism of the formation of urea has shown, as expected, that mercuric oxide plays no part in its production; thus, when mixtures of oxamide and mercuric oxide in different proportions were heated to the temperature (230—240°) at which the oxide was completely reduced, no urea could be detected in the product (Expt. I).

When oxamide was heated to a temperature just sufficient to effect complete volatilisation, ammonium cyanate, urea, and biuret were found in the sublimate, whilst ammonia, water, carbon monoxide, and hydrogen cyanide were evolved.

\* It was not possible to consult the original paper.

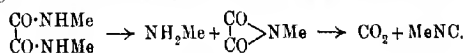
The decomposition is brought about as follows:



Since ammonia was first evolved (at about 110°) whether mercuric oxide was present or not, it is evident that the formation of urea from oxamide, in accordance with (a), is but another example of Wöhler's synthesis.

The respective yields of ammonium cyanate and of urea were 2.9 and 4.18 per cent. of the theoretical when oxamide was rapidly heated and the vapours quickly condensed by artificial cooling. When the amide was slowly heated without further precaution, the yields were 2.4 and 2.6 per cent. respectively, whilst the formation of hydrogen cyanide was more evident than in the former case (Expts. II, III, IV, and V). The formation of biuret is accounted for by the above explanation of the mechanism of the decomposition.

It may be mentioned that when *s*-dimethyloxamide was heated with mercuric oxide to 240°, no dimethylurea was formed; when the amide was heated alone, whilst the greater part volatilised unchanged, there was decomposition, represented by the scheme:



This change is being further investigated.

#### EXPERIMENTAL.

*Expt. I.*—An intimate mixture of 1.76 grams of oxamide and 4.32 grams of mercuric oxide was heated in a test-tube partly immersed in glycerol. Ammonia was evolved at 110°, and at 230–240° the colour of the mixture changed to grey and the heating was stopped. The cold residue was extracted with 10 c.c. of water, but no urea could be detected in the solution, even by means of the extremely delicate xanthhydrol test. The experiment was repeated, with different proportions of the two substances, with a similar result.

*Expt. II.*—Two grams of oxamide were heated in a hard glass tube held horizontally until the whole had sublimed. The sublimate

was extracted with cold water, and to the solution 10 c.c. of *N*/10-silver nitrate were added, 5.65 c.c. being required for the precipitation of the ammonium cyanate present, which was therefore equal to 2.49 per cent.

*Expt. III.*—The above experiment was repeated, but the forepart of the tube was cooled with a circular current of water; 6.8 c.c. of *N*/10-silver nitrate were required; hence 2.9 per cent. of the theoretical amount of ammonium cyanate was present.

*Expts. IV and V.*—Two grams of oxamide were heated as in Expt. II, the aqueous extract, after removal of 'cyanate,' being evaporated to dryness. The urea extracted by alcohol from the residue gave 6.66 c.c.  $N_2$  at N.T.P. on decomposition with alkaline sodium hypobromite = 2.61 per cent. of the theoretical; 10.68 c.c.  $N_2$  at N.T.P. were obtained from the urea produced under the conditions of Expt. III, which corresponds with 4.18 per cent. of the theoretical amount.

#### *Summary.*

(1) Urea is not formed when a mixture of oxamide and mercuric oxide is heated to the stage at which the oxide is completely reduced.

(2) The synthesis of urea from oxamide is the result of the generation of cyanic acid and ammonia from the decomposition of the amide.

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## LXI.—*A New Method for the Determination of Conductivity.*

By EDGAR NEWBERY.

THE convenience and simplicity of Kohlrausch's method for the determination of the conductivity of aqueous solutions has been so long recognised that at the present time no trustworthy data on this subject exist which have not been obtained by the above method or some slight modification of it.

Further, all conductivity vessels are standardised with the aid of the original values given by Kohlrausch for potassium chloride solutions.

A critical examination of the method shows, however, that it is

E E\*

based on several assumptions which have not so far been experimentally proved correct. The following are the chief objections to the method.

(1) It is assumed that by using alternating current, all polarisation effects are eliminated.

Taylor and Acree (*J. Amer. Chem. Soc.*, 1916, **38**, 2396 *et seq.*) have studied this subject, and have shown that consistent results with simple electrolytes can only be obtained by using a perfect sine wave current and extrapolating the results thus obtained to determine the conductivity when the frequency is infinite. It appears probable, therefore, that with these precautions polarisation is absent in the case of simple electrolytes, such as potassium chloride, but when certain other electrolytes are used, especially with insufficiently platinised electrodes, it is by no means certain that decomposition of the electrolyte, with consequent polarisation of the electrodes, does not occur. To quote an extreme case, an alternating current passed between copper electrodes in a concentrated solution of potassium cyanide dissolves the copper with the same efficiency as direct current when the frequency is not greater than 1000 per minute, and with an efficiency of 33 per cent. when the frequency is 38,000 per minute. Since very small traces of polarisation may exert very great influence on the measured conductivity, it follows that grave doubt is thrown on the trustworthiness of many of our present conductivity data.

(2) It is assumed that conductivity is independent of current density, current concentration, and type of current (direct or alternating). Whilst this is probably true in general, it has not been sufficiently investigated to be relied on in all cases.

(3) Errors are introduced by self-induction, electrostatic capacity, shape of conductivity vessel, etc., the corrections for which are troublesome and of doubtful accuracy.

It is therefore very desirable to devise a method of measuring conductivity which will utilise direct current and completely eliminate the effect of polarisation at the electrodes.

#### EXPERIMENTAL.

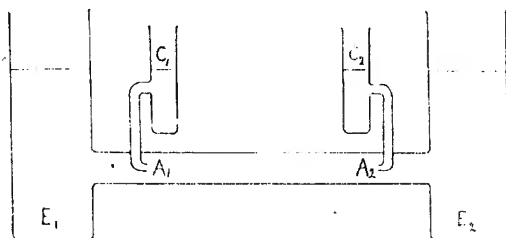
The method described is a simple modification of a common method for measuring the resistance of a metallic conductor by determining the fall of potential along it during the passage of a known current.

Altogether, seven different forms of the apparatus were constructed, but the principle of them all may be seen from Fig. 1, which shows the most convenient form for general use in obtain-

ing relative values, and Fig. 2, which shows the most accurate form for the determination of absolute values.

In using the first form of apparatus, a small but constant current is passed between the electrodes  $E_1E_2$ , along the tube  $A_1A_2$ , and also through a standard resistance. Standard electrodes (calomel, mercurous sulphate, etc.) are constructed in the vessels  $C_1C_2$ , and these are connected with an accurate dial potentiometer reading to five significant figures. The extremities of the standard resistance are also connected to the same potentiometer, and by means of a commutator, the fall of potential along the tube  $A_1A_2$  and across the terminals of the standard resistance may be measured

FIG. 1.



in rapid succession. The specific conductivity of the electrolyte is then given by

$$K = \frac{D^2}{VE} \times \frac{y}{x},$$

where  $D$  is the distance between the electrode tips  $A_1A_2$ ,  $V$  the volume of the liquid in the tube between the same points,  $E$  the standard resistance, and  $x$  and  $y$  the potential differences between the electrodes  $C_1C_2$  and between the terminals of the standard resistance respectively. All measurements described were carried out with the apparatus immersed in a thermostat at  $25^\circ$ .

#### *Conductivity of N-Potassium Chloride at $25^\circ$ .*

For this purpose, the apparatus shown in Fig. 2 was used. A burette (50 c.c.) was chosen out of a large number such that the graduations were as uniform as possible, and carefully calibrated by a weighing method with mercury, the exact distance between the first and last markings being determined with the cathetometer. (These measurements were repeated after construction of the apparatus.) The tap was then cut off, standard electrode



vessels were sealed on as shown, with the tips central and exactly opposite the end graduations, and large side-tubes,  $B_1B_2$ , sealed on well behind the electrode tips. These side-tubes were connected with the main electrode vessels  $E_1E_2$ .

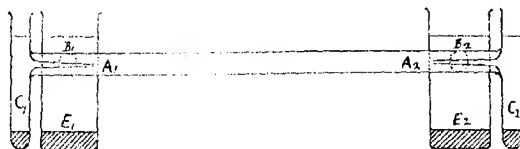
Errors due to expansion of the glass, irregularities in the tube etc., were calculated and found to amount to not more than 0.001 per cent.

The electrodes used in all four vessels were calomel, great care being taken to secure purity of mercury and calomel. Before use the electrodes  $C_1C_2$  were connected through a sensitive galvanometer. If any deflexion was observed, they were short-circuited for some time until no difference of potential could be detected.

The main electrode vessels were 8 cm. high and 5 cm. in diameter the mouths being closed with well-fitting corks to prevent evaporation.

The standard resistance, 99.84 ohms, and the thermometer used were calibrated at the National Physical Laboratory. The

FIG. 2.



galvanometer was a moving coil instrument sensitive to  $10^{-9}$  ampere

By varying the strength of the main current between 0.1 and 5 milliamperes, readings were taken on very varied portions of the potentiometer.

By repeatedly changing the direction of the main current, errors due to concentration changes in the electrolyte and inequality of potential between  $C_1$  and  $C_2$  were eliminated. By experiment with other forms of the apparatus, using different lengths of tube and different sized electrode tips, it was found that errors due to uneven flow of current in the immediate neighbourhood of the electrode tips are not greater than 0.01 per cent, if the diameter of these tips is not more than 0.1 of that of the main tube.

The chief difficulty experienced in all these experiments lay in securing a perfectly constant main current. The use of calomel electrodes of large area and small currents was so far successful in this case in overcoming this difficulty that long series of closely agreeing results were easily obtained. Other devices for the same purpose are described later.

*Purification of Materials.*—The water was redistilled, using a tin condenser, and had a conductivity of  $0.5 \times 10^{-6}$  mhos.

The mercury was redistilled and sprayed through dilute nitric acid several times before use.

The calomel was washed with water and well triturated with mercury and potassium chloride solution several times before being placed in the apparatus.

The potassium chloride was a special product, guaranteed pure by the manufacturers. This was precipitated from a saturated solution by means of hydrogen chloride, dried, and heated to dull redness, and again precipitated from a hot saturated solution in conductivity water by rapid cooling. After drying and heating to dull redness, it was weighed out and the solution made up at  $18^{\circ}$  to the strength used by Kohlrausch (74.59 grams per litre at  $18^{\circ}$ ). This solution was made up, *ab initio*, three times, starting with different samples of the original salt, and no difference in conductivity could be detected in the three solutions.

The solution was exactly neutral to indicators, and no trace of sulphate, carbonate, phosphate, or nitrate could be detected by the usual tests. Quartz vessels were used wherever possible in the preparation of the salt, and all glass vessels were well steamed out shortly before use to avoid the introduction of sodium silicate. The flame spectrum showed the sodium lines somewhat feebly, but no other ingredient. Since the presence of as much as 1 per cent. of sodium chloride in the potassium salt would only raise the conductivity of the solution by 0.05 per cent., it is improbable that any appreciable error exists due to impurity of the original salt.

*Results.*—The readings were generally taken in sets of ten, the potential fall along the tube and the standard resistance being taken in alternate order to compensate for slight changes in the main current. After reversal of the current, another set of ten pairs of readings was taken. The current was then broken and the apparatus left for a few hours before repeating the observations. The whole was then cleaned out, dried, and refilled with fresh solution.

Of 100 results thus obtained for the specific conductivity of *N*-potassium chloride, 20 gave the value 0.1126 mho., 29 gave the value 0.1125 mho., and 51 gave 0.1124 mho. at  $25^{\circ}$ .

The average value is therefore 0.11247 mho., which is higher than that given by Kohlrausch by 0.6 per cent. Since the current used by Kohlrausch was obtained from a small induction coil, which does not give a symmetrical alternating current, polarisation effects were probably present, and his result is probably too low. It is

unlikely that the error in the present work exceeds 0.1 per cent., and 0.1125 is therefore nearer the true value than 0.1118.

*Sodium Chloride Saturated at 25°.*—Similar precautions were taken to secure purity of materials as in the case of potassium chloride.

The solution was made by shaking excess of the pure salt with conductivity water at 60° for fifteen minutes, and allowing to remain with occasional shaking for twenty-four hours in a thermostat at 25°. Calomel electrodes were used as before.

The final value obtained was 0.2520(5), which is greater than that given by Kohlrausch by 0.3 per cent.

*N-Silver Nitrate (169.89 grams per litre at 18°).*—The main electrodes in this case were plates of pure assay silver, "1000 quality." Secondary electrodes of the same material were tried, but were not so satisfactory as calomel electrodes with a connecting liquid of *N*-potassium nitrate.

The value obtained for the specific conductivity was 0.07796 mho. at 25°.

The value calculated from that of Kohlrausch and Steinwehr (*Sitzungsber. K. Akad. Wiss. Berlin*, 1902, 587) by means of the temperature coefficients given by Déguisne (*Diss.*, Strassburg, 1895) is 0.0779 mho. at 25°.

*N-Sulphuric Acid (49.043 grams per litre at 18°).*—The purest available materials were used, and the acid was estimated gravimetrically by precipitation with barium chloride and volumetrically by titration with sodium carbonate.

Mercurous sulphate electrodes were used for both primary and secondary electrodes, and were found to be satisfactory only if used within twenty-four hours of making up. After this time, the mercurous salt gradually dissolves in the acid, increasing its conductivity by 0.1 per cent. in three days, and still more on longer keeping. This raises doubts as to the trustworthiness of the mercurous sulphate electrode for prolonged investigations. No change could be detected within the first twenty-four hours.

The value obtained for the specific conductivity was 0.2137 mho. at 25°.

Kohlrausch gives the value 0.1980 mho. and Loomis (*Ann. Phys. Chem.*, 1897, [iii], 60, 547) gives 0.195 mho., both at 18°. Using Gotrian's data for temperature coefficient (*Ann. Phys. Chem.*, 1874, [ii], 151, 378), these give the values 0.2220 and 0.2186 respectively at 25°, which exceed the value found here by 3.6 and 2.2 per cent, respectively.

*Summary.*

A form of conductivity apparatus is described in which direct current is used and disturbing effects of polarisation at the electrodes are eliminated.

The following values have been obtained for the specific conductivity of solutions in mhos. at 25°:

*N*-Potassium chloride (74.59 grams per litre at 18°), 0.1124(7).

Sodium chloride saturated at 25°, 0.2520(5).

*N*-Silver nitrate (169.89 grams per litre at 18°), 0.07796.

*N*-Sulphuric acid (49.043 grams per litre at 18°), 0.2137.

In conclusion, the author wishes to thank Prof. A. Lapworth for his interest in this work.

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LXII.—*The Abnormality of Strong Electrolytes. Part III. The Osmotic Pressure of Salt Solutions and Equilibrium between Electrolytes.*

By JNANENDRA CHANDRA GHOSH.

In the previous papers (this vol., pp. 449, 627) it has been shown that the number of free ions in a given solution containing a gram-molecule of salt is

$$n \cdot N \cdot e^{-\frac{A}{nRT}} \dots \dots \dots (1)$$

where *N* is Avogadro's number, *n* is the number of ions into which a molecule dissociates, and *A* is the work required to separate the component ions of a gram-molecule to an infinite distance apart at that particular dilution. It has also been established that only these free ions take part in the conduction of electricity through solutions.

An equation of state free from any arbitrary assumption was deduced by Clausius (*Phil. Mag.*, 1870, [iv], 40, 122; Jeans, "Dynamical Theory of Gases," 2nd edition, pp. 141—145) from purely dynamical principles, which takes into account the forces of molecular attraction. His theorem  $PV = \frac{2}{3}$  kinetic energy —  $\frac{1}{3}$  virial is specially suitable for application to salt solutions, since

the work necessary to overcome the forces of electrical attraction in this case can be easily calculated. Milner (*Phil. Mag.*, 1912, [vi], **23**, 551; 1913, **25**, 747) has already developed a method for calculating the virial of solutions of univalent binary electrolytes, and has shown that the Clausius theorem agrees well with experimental results. No relation between the activity coefficient  $\frac{\mu_v}{\mu_\alpha}$  and the osmotic pressure of salt solutions has, however, yet been established on the basis of complete ionisation at all dilutions. We have seen that the molecular conductivity is proportional to the number of free ions,  $n.N.e^{-\frac{A}{nRT}}$ . Since at infinite dilution  $A=0$ ,

$$\frac{\mu_v}{\mu_\alpha} = e^{-\frac{A}{nRT}},$$

or

$$A = nRT \log_e \frac{\mu_\alpha}{\mu_v} \dots \dots \dots (2)$$

which holds good for all types of salt solutions. Here  $A$ , of course, is the virial, and  $PV$  thus becomes equal to

$$\begin{aligned} nRT - \frac{1}{2}nRT \log_e \frac{\mu_\alpha}{\mu_v}, \\ = nRT \left\{ 1 - \frac{1}{2} \log_e \frac{1}{\alpha} \right\}, \end{aligned}$$

or

$$i = n \cdot \left\{ 1 - \frac{1}{2} \log_e \frac{1}{\alpha} \right\} \dots \dots \dots (3)$$

According to Arrhenius, on the view that in a solution we have an equilibrium between ions and undissociated molecules,

$$i = 1 + (n-1)\alpha \dots \dots \dots (4)$$

At infinite dilution, equations (3) and (4) lead to the same limiting value of  $i=n$ . At other dilutions, the two equations give different results. In this paper it is proposed to examine which of these equations agrees best with actual observations.

#### *Determination of $\alpha$ for Univalent Binary Electrolytes at Various Dilutions.*

It has already been shown that the variation of activity-coefficient with dilution for univalent binary electrolytes is given by the equation

$$\frac{N \cdot E^2 \cdot \sqrt[3]{2N}}{D \cdot \sqrt[3]{V}} = 2RT \log_e \frac{\mu_\alpha}{\mu_v} = 2RT \log_e \frac{1}{\alpha}.$$

The agreement with the observed values is quite satisfactory for dilutions of 10 litres and upwards (Part I). This coincidence becomes, however, less perfect as the concentration increases. This is certainly due to the fact, suggested by Washburn (*J. Amer. Chem. Soc.*, 1911, **33**, 1464), and later emphasised by Noyes and Falk (*ibid.*, 1912, **34**, 458), that the ratio  $\frac{\mu_v}{\mu_\alpha}$  is not a true measure of the activity-coefficient. A correction for change in ionic mobility, due to the change in the viscosity of solutions with dilution, is necessary; the ratio  $\frac{\mu_v \eta_v}{\mu_\alpha \eta_\alpha}$ , furnishes a much closer approximation to the true values of the activity-coefficient than the ratio  $\frac{\mu_v}{\mu_\alpha}$ . Taking into account this correction for viscosity, the equation for univalent binary electrolytes becomes

$$A = \frac{N \cdot R^2 \cdot \sqrt[3]{2N}}{D \cdot \sqrt[3]{V}} = 2RT \log_e \frac{\mu_\alpha \eta_\alpha}{\mu_v \eta_v} = 2RT \log_e \frac{1}{\alpha} \quad (5)$$

From table I it will be evident that, with this modification, the above equation can be very well applied to concentrations up to 0.5*N*. In the table, the values of  $\mu_v$  and  $\eta_v$  have been taken from the paper of Noyes and Falk (*loc. cit.*). The striking regularity brought to notice by these investigators, that salts of analogous constitution have the same activity-coefficient at the same dilution, is, of course, a necessary deduction of the above equation. Above 0.5*N*, the volume actually occupied by the solute molecules is not negligible.

TABLE I. T=18°.

Salt.	Extra- polation value of $\mu_{\infty} \eta_{\infty}$	Calc. value of $\mu_{\infty} \eta_{\infty}$ from $\mu_{10} \eta_{10}$	$v =$				
			2.	5.	10.	20.	
1. NaCl	108.9	109.8	$\left\{ \begin{array}{l} \mu_v \eta_v \text{ calc.} \\ \mu_v \eta_v \text{ obs.} \end{array} \right.$	82.3 84.2	88.8 89.1	92.7 92.7	96.1 96.1
2. KCl	130.0	132.5	$\left\{ \begin{array}{l} \mu_v \eta_v \text{ calc.} \\ \mu_v \eta_v \text{ obs.} \end{array} \right.$	99.2 101.3	107.0 107.5	111.8 111.8	115.8 115.6
3. LiCl	98.8	99.0	$\left\{ \begin{array}{l} \mu_v \eta_v \text{ calc.} \\ \mu_v \eta_v \text{ obs.} \end{array} \right.$	74.2 75.5	80.0 80.2	83.6 83.6	86.7 86.6
4. KBr	132.2	134.5	$\left\{ \begin{array}{l} \mu_v \eta_v \text{ calc.} \\ \mu_v \eta_v \text{ obs.} \end{array} \right.$	101.0 101.3	108.6 109.1	113.5 113.5	117.6 117.4
5. KI	131.2	133.8	$\left\{ \begin{array}{l} \mu_v \eta_v \text{ calc.} \\ \mu_v \eta_v \text{ obs.} \end{array} \right.$	100.1 101.4	— —	112.9 112.9	116.9 116.7

It will be observed that the difference between the calculated value of  $\mu_\alpha$  and the extrapolation value, obtained by means of empirical equations, is within 2 per cent.

TABLE II.

	$V=2$ .	5.	10.	20.	50.	100.
Theoretical value of $\alpha$ for all univalent binary electrolytes according to equation 5. Per cent.....	74.8	80.8	84.4	87.5	90.6	92.4

*Variation of  $\alpha$  with Dilution for Ternary Electrolytes.*

For ternary electrolytes, the variation of activity-coefficient with dilution is very satisfactorily represented by the equation

$$\frac{6N \cdot E^2 \cdot \sqrt[3]{2N}}{D \cdot \sqrt[3]{3} \cdot \sqrt[3]{V}} = 3RT \log_e \frac{\mu_x}{\mu_p} = 3RT \log_e \frac{1}{\alpha}.$$

In table III, the percentage values of  $\alpha$ , calculated from the above equation for various dilutions, are given.

TABLE III.

$v =$	10.	20.	40.	50.	100
$\alpha =$	87.8	73.5	78.3	79.7	84.0

*Determination of the Value of  $i$  for Univalent Binary Electrolytes.*

The method of determining  $i$  with sufficient exactness is based on observations on the lowering of the freezing point of salt solutions. Attempts were made to determine  $i$  from the diminution of the vapour pressure of solutions (compare Menzies, *Zeitsch. physikal. Chem.*, 1911, **76**, 231), but until the recent work of Lovelace, Frazer, and Miller (*J. Amer. Chem. Soc.*, 1916, **38**, 515) the methods were not sufficiently accurate. These investigators have succeeded in improving the technique of the method to such an extent that the temperature of the bath can be kept constant within  $0.001^\circ$  for more than twelve hours, and a pressure of  $0.0001$  mm. can be exactly measured. The results obtained by them are rather peculiar, inasmuch as the molecular lowering of the vapour pressure of a solution of potassium chloride remains constant as the concentration changes from  $2N$  to  $0.2N$ . Any opinion on these results must at present be suspended, as the work is still in progress.

The method based on the lowering of the freezing point has been well investigated, and all the observations, with the exception of those of Ponsot (*Ann. Chim. Phys.*, 1897, [vii], **10**, 79; 1899, **16**, 162), go to show that  $i$  continually increases until the limiting

value  $n$  is reached. Noyes and Falk, in their valuable paper on the properties of salt solutions (*J. Amer. Chem. Soc.*, 1910, **32**, 1020), have given a fairly complete account of the investigations on the lowering of the freezing point up to that time. They have not attached the same weight to the data obtained by different investigators, and hence their mean value of  $i$  is somewhat arbitrary. In table IV I have recalculated the mean value of the molecular lowering of the freezing point on the simpler, but still arbitrary, basis that the probable error of the various investigators is approximately the same. The value of  $i$  is obtained by dividing the mean molecular lowering of the freezing point by 1.858. In the footnote are given the references to the work of the investigators whose data have been utilised in calculating the mean value of  $i$ .

The weighted mean of the "molecular number  $i$ " for salts of the uni-univalent type, obtained by Noyes and Falk (*loc. cit.*, p. 1027), is included in table VIII for the sake of comparison. It should be noted that this mean was obtained by excluding the data on the molecular numbers of lithium chloride and sodium bromide. The values of  $i$  for these salts, as will be seen from table IV, are always higher than the mean. For ternary electrolytes, Noyes and Falk do not give any weighted mean, but observe that "the values of the molecular numbers are of similar magnitude, the range being 2.57 to 2.68 at dilution 10 and 2.71 to 2.77 at dilution 50."

TABLE IV.

Salt.	$V=2$ .	5.	10.	20.	50.	100.
KCl <sup>1</sup>	1.800	1.833	1.862	1.886	1.922	1.947
NaCl <sup>2</sup>	1.824	1.850	1.880	1.897	1.928	1.945
LiCl <sup>3</sup>	—	—	1.901	1.912	1.928	1.937
CsCl <sup>4</sup>	1.780	—	1.878	1.892	1.930	—
NaBr <sup>4</sup>	—	1.871	1.891	1.911	—	—
KBr <sup>4</sup>	1.813	1.841	1.870	1.910	1.929	—

<sup>1</sup> Jones, *Zeitsch. physikal. Chem.*, 1893, **11**, 110; **12**, 639. Loomis, *Ann. Phys. Chem.*, 1894, [iii], **51**, 500; 1896, **57**, 495; 1897, **60**, 523; *Zeitsch. physikal. Chem.*, 1900, **32**, 578; 1901, **37**, 406. Lewis, *ibid.*, 1894, **15**, 365. Abegg and Nernst, *ibid.*, 1894, **15**, 681; 1896, **20**, 207. Whetham, *ibid.*, 1900, **33**, 344. Raoult, *ibid.*, 1898, **27**, 617. Jahn, *ibid.*, 1905, **50**, 129; 1907, **31**, 31. Richards, *ibid.*, 1903, **44**, 563. Ponsot, *loc. cit.* Bedford, *Proc. Roy. Soc.*, 1910, [A], **83**, 454.

<sup>2</sup> Jones, Loomis, Raoult, Ponsot, Abegg, Jahn, Hausrath, *Ann. Physik.*, 1902, [iv], **9**, 522. Osaka, *Zeitsch. physikal. Chem.*, 1902, **41**, 560.

<sup>3</sup> Loomis, Jahn.

<sup>4</sup> Jahn, Biltz, *Zeitsch. physikal. Chem.*, 1902, **40**, 185.

<sup>5</sup> Jahn.

<sup>6</sup> Jahn, Biltz.



TABLE V.

Mean value of  $i$  for univalent binary electrolytes at various dilutions.

$v =$	2.	5.	10.	20.	50.	100.
$i =$	1.805	1.849	1.880	1.900	1.935	1.942

*Determination of  $i$  for Ternary Electrolytes at Various Dilutions.*

In calculating the value of  $i$ , the method described before has been followed. Table VI contains the mean value of  $i$  for some well-investigated ternary electrolytes at various dilutions.

TABLE VI.

Salt.	Mean value of $i$ .	$v = 10.$	20.	50.
$\text{CaCl}_2^1$ .....	$i =$	2.624	2.685	2.789
$\text{MgCl}_2^1$ .....	$i =$	2.677	2.708	2.763
$\text{SrCl}_2^1$ .....	$i =$	2.629	2.673	2.781
$\text{BaCl}_2^4$ .....	$i =$	2.580	2.640	2.712
$\text{ZnCl}_2^5$ .....	$i =$	2.579	2.666	2.771
$\text{CO}(\text{NO}_2)^6$ ...	$i =$	2.700	2.760	—
$\text{Cu}(\text{NO}_3)^7$ ...	$i =$	2.630	2.730	—
$\text{Ni}(\text{NO}_3)_2^8$ ...	$i =$	2.600	2.670	2.810

<sup>1</sup> Loomis, Ponsot, Jones and Pearce. <sup>2</sup> Loomis. <sup>3</sup> Loomis, Jones and Pearce. <sup>4</sup> Bedford, Loomis, Jones, Ponsot, Whetham. <sup>5</sup> Jones. <sup>6</sup> Jones and Pearce. <sup>7</sup> Jones and Pearce. <sup>8</sup> Jones and Pearce.

TABLE VII.

Mean value of  $i$  for ternary electrolytes at various dilutions.

$v =$	10.	20.	50.
$i =$	2.620	2.691	2.771

*The Validity of the Clausius Theorem.*

TABLE VIII.

	$v = 2.$	5.	10.	20.	50.	100.
$i$ According to Noyes and Falk .....	1.804	1.837	1.865	1.887	1.925	1.937
$i$ Observed for univalent binary salts .....	1.805	1.849	1.880	1.900	1.935	1.942
$i$ According to equation 3 .....	1.806	1.859	1.887	1.910	1.934	1.947
$i$ According to equation 4 .....	1.748	1.808	1.844	1.875	1.906	1.924

TABLE IX.

	$v = 10.$	20.	50.
$i$ Observed for ternary salts .....	2.620	2.691	2.771
$i$ According to equation 3 .....	2.616	2.695	2.773
$i$ According to equation 4 .....	2.356	2.470	2.594

It is evident that the equation ·

$$i = n \left( 1 - \frac{1}{2} \log_e \frac{\mu_{\alpha}}{\mu_{\beta}} \right),$$

based on the Clausius theorem, agrees best with the experimental results. The Arrhenius equation fails conspicuously in the case of ternary electrolytes. Jones attempted to explain this anomaly by his hydrate theory. The high value of  $i$  according to him, is due to the fact that the solvent combines with the solute, the ratio of solute to solvent molecules increases, and hence  $i$  becomes abnormally large. His theory may be correct for concentrated solutions. There is, however, some inherent improbability in the fact that in dilute solutions about 150 water molecules must be made to combine with an ion in order that the difference between the observed value of  $i$  and that calculated from Arrhenius's equation may be explained. The hydrate theory of dilute solutions becomes simply unnecessary in view of the complete validity of the Clausius theorem as applied to salt solutions.

#### *Activity-coefficient of Salts in Mixed Solutions.*

Here we have the following empirical rule: "The conductivity and the freezing-point lowering of a mixture of salts having one on in common are those calculated under the assumption that the degree of ionisation (activity-coefficient) of each salt is that which it would have if it were present alone at such an equivalent concentration, that the concentration of either of its ions is equal to the sum of the equivalent concentrations of all the positive or negative ions present in the mixture" (A. A. Noyes, *Tech. Quart.*, 1904, 17, 301).

Let there be two solutions of sodium chloride and potassium chloride, and let their equivalent dilutions be  $V$  and  $V'$  respectively. If  $X$  and  $Y$  are their respective activity-coefficients, then

$$\log \frac{1}{x} = k \left( \frac{1}{V} \right)^{\frac{1}{2}},$$

and

$$\log \frac{1}{y} = k \left( \frac{1}{V'} \right)^{\frac{1}{2}}.$$

If the two solutions are mixed together, the total volume =  $V + V'$ . But, on mixing, there is a distribution of arrangement until the entire solution is uniform. Since there are only ions in a solution, and since the arrangement in sodium chloride and potassium chloride solutions is identical, the distance between the sodium and chlorine ions in an electric doublet is the same as it would have

been if the dilution were  $\frac{V+V'}{1+1}$ . The result is that the activity-coefficient of sodium chloride in the mixture corresponds with that of the pure solution at dilution  $\frac{V+V'}{2}$ , which is the equivalent dilution of the common ion. The same is true for potassium chloride. On mixing, therefore,

$$\log \frac{1}{x'} = k \left( \frac{2}{V+V'} \right)^{\frac{1}{2}},$$

$$\log \frac{1}{y'} = k \left( \frac{2}{V+V'} \right)^{\frac{1}{2}}.$$

where  $x'$  and  $y'$  are the respective activity-coefficients of the salts in the mixture.

Therefore  $X'=Y'$ , or the activity-coefficient of each of the salts is the same and corresponds with that of a solution the equivalent concentration of which is equal to the sum of the equivalent concentrations of all the positive or negative ions present in the mixture.

If  $V=V'$ , that is, if the initial concentration of both solutions is the same,

$$\frac{1}{V} = \frac{1}{V'} = \frac{1+1}{V+V'},$$

therefore  $X=Y=X'=Y'$ . That is, the activity-coefficient does not change when two salt solutions having the same equivalent concentration are mixed. This is the condition for isohydry.

#### Conclusions.

In this series of papers on the abnormality of strong electrolytes, I have proceeded on the following assumptions:

(1) A salt solution is always completely ionised, the force of attraction between ions being governed by the law of inverse squares.

(2) The arrangement of ions in a univalent binary electrolyte corresponds with a simple cubic lattice, whilst in a solution of a ternary electrolyte the arrangement corresponds with a fluorspar lattice.

The following equations have been derived:

$$\text{I. } A = \frac{N \cdot E^2 \cdot \sqrt[3]{2N}}{D \cdot \sqrt{V}} = 2RT \log_e \frac{\mu_{\alpha}}{\mu_{\nu}} \quad \dots \text{ for universal binary salts.}$$

$$\text{II. } A = \frac{6N \cdot E^2 \cdot \sqrt[3]{2N}}{D \cdot \sqrt{3} \cdot \sqrt[3]{V}} = 3RT \log_e \frac{\mu_{\alpha}}{\mu_{\nu}} \quad \dots \text{ for ternary salts.}$$

$$\text{III. } i = n \left\{ 1 - \frac{1}{2} \log_e \frac{\mu_{\alpha}}{\mu_{\nu}} \right\}$$

The validity of these fundamental equations has been completely demonstrated both in aqueous and non-aqueous solutions. The variation of the activity-coefficient with temperature has been successfully calculated, and the conditions for isohdry have been determined. In fact, a complete theory of dilute salt solutions has been propounded.

My best thanks are due to Prof. P. C. Rây and to my friend and colleague Mr. J. N. Mukherjee, M.Sc.

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### LXIII.—*The Preparation of certain Organic Stanno- and Stanni-chlorides.*

By JOHN GERALD FREDERICK DRUCE.

DOUBLE haloids of tin with organic bases have long been known. Thus Cook (*Amer. Chem. J.*, 1899, **22**, 435) described a number of aliphatic amine salts, and Slagle (*ibid.*, 1898, **20**, 633) prepared the aniline and toluidine compounds. Pyridine stannochloride has been described by Hayes (*J. Amer. Chem. Soc.*, 1902, **24**, 360), and pyridine stannichloride by Weinland and Barnes (*Zeitsch. anorg. Chem.*, 1909, **62**, 250). The quinoline salts have been isolated by Borsbach (*Ber.*, 1890, **23**, 431).

These salts were usually prepared from hydrochloric acid solutions of the component haloids, and the same method of preparation has been employed in the case of the new compounds described below.

#### EXPERIMENTAL.

*Diethylamine Stannochloride*,  $(\text{NHEt}_2)_2\text{H}_2\text{SnCl}_4$ .—This salt was isolated from a dilute hydrochloric acid solution containing two molecular proportions of amine to one of stannous chloride. The crystals which separated were collected and dried on a porous plate in a desiccator over sodium hydroxide. The salt was very deliquescent and melted at  $58^\circ$ :

0.9852 gave 0.3640  $\text{SnO}_2$ .  $\text{Sn} = 29.11$ .

0.5950 „ 0.8355  $\text{AgCl}$ .  $\text{Cl} = 34.75$ .

$(\text{C}_4\text{H}_{11}\text{N})_2\text{H}_2\text{SnCl}_4$  requires  $\text{Sn} = 29.04$ ;  $\text{Cl} = 34.69$  per cent.

*o*-Toluidine Stannochloride,  $(C_7H_7NH_2)_2, H_2SnCl_4$ .—*o*-Toluidine (5.35 grams) was added to 100 c.c. of a dilute hydrochloric acid solution containing 5.65 grams of stannous chloride, and warmed. On cooling, fine, silky needles, melting at  $164^\circ$ , were deposited.

The salt dissolved readily in cold water, the solution remaining clear unless boiled:

0.4385 gave 0.1382  $SnO_2$ .  $Sn = 24.82$ .

0.1205 „ 0.1454  $AgCl$ .  $Cl = 29.85$ .

$(C_7H_7N)_2, H_2SnCl_4$  requires  $Sn = 24.90$ ;  $Cl = 29.75$  per cent.

*o*-Toluidine Stannichloride,  $(C_7H_7N)_2, H_2SnCl_6, H_2O$ .—This compound was obtained in very pale pink, short needles, which began to decompose at  $210^\circ$ :

0.8247 gave 0.2274  $SnO_2$ .  $Sn = 21.23$ .

0.1228 „ 0.1841  $AgCl$ .  $Cl = 37.39$ .

$(C_7H_7N)_2, H_2SnCl_6, H_2O$  requires  $Sn = 21.01$ ;  $Cl = 37.64$  per cent.

Methylaniline Stannochloride,  $C_7H_9N, HSnCl_3$ .—Redistilled methylaniline (5.35 grams) and stannous chloride (5.65 grams) were dissolved together in 100 c.c. of hot dilute hydrochloric acid. The clear solution deposited a mass of short, stout, colourless prisms dissolving in water to a clear solution, which became turbid only on boiling. The salt is also soluble in alcohol, but not in chloroform, and melts at  $106^\circ$ :

0.2549 gave 0.1157  $SnO_2$ .  $Sn = 35.75$ .

0.3264 „ 0.4224  $AgCl$ .  $Cl = 32.02$ .

$C_7H_9N, HSnCl_3$  requires  $Sn = 35.63$ ;  $Cl = 31.93$  per cent.

Methylaniline Stannichloride,  $(C_7H_9N)_2, H_2SnCl_6$ .—Molecular proportions of the base and hydrated crystalline stannic chloride were dissolved together in dilute hydrochloric acid. Colourless crystals of the stannichloride, melting and decomposing at  $251^\circ$ , separated from the solution. The salt dissolved in water to a clear solution, which was not appreciably hydrolysed even when boiled:

0.5054 gave 0.1401  $SnO_2$ .  $Sn = 21.78$ .

0.1728 „ 0.2703  $AgCl$ .  $Cl = 38.71$ .

$(C_7H_9N)_2, H_2SnCl_6$  requires  $Sn = 21.67$ ;  $Cl = 38.84$  per cent.

Chlorination of a dilute hydrochloric acid solution of the stannochloride also gave this compound, but the product was not pure and had a low melting point.

*m*-Phenylenediamine Stannochloride,  $C_6H_4(NH_2)_2, 2HSnCl_3$ .—This compound was obtained by reducing *m*-nitroaniline or *m*-dinitrobenzene with tin and hydrochloric acid. It forms fine, silky prisms, melting at  $128^\circ$ , which are soluble in water, but the

solution soon becomes cloudy. Dilute hydrochloric acid solutions of the salt gave the reactions for stannochlorides, for example, iodine solutions were decolorised; a white precipitate was obtained with mercuric chloride solution, which darkened on warming, and a dark brown precipitate of stannous sulphide was obtained by passing in hydrogen sulphide:

0.4211 gave 0.2232  $\text{SnO}_2$ .  $\text{Sn} = 41.75$ .

0.4537 „ 0.6891  $\text{AgCl}$ .  $\text{Cl} = 37.58$ .

$\text{C}_6\text{H}_5\text{N}_2\cdot 2\text{HSnCl}_3$  requires  $\text{Sn} = 41.85$ ;  $\text{Cl} = 37.97$  per cent.

*m-Phenylenediamine Stannichloride*,  $\text{C}_6\text{H}_5\text{N}_2\cdot \text{H}_2\text{SnCl}_6$ .—Dilute hydrochloric acid solutions of the above stannochloride were oxidised to stannochloride on exposure to air, but the crystals isolated from these solutions were not pure. The pure salt was obtained from *m*-nitroaniline (2.56 grams) or from *m*-dinitrobenzene (1.3 grams) and stannous chloride (10.5 grams). Almost colourless crystals of the stannichloride separated from the hydrochloric acid solution. It dissolved readily in cold water, and the solution did not hydrolyse unless heated. The crystals melted and decomposed at  $265^\circ$ :

0.4762 gave 0.1606  $\text{SnO}_2$ .  $\text{Sn} = 26.56$ .

0.4511 „ 0.8767  $\text{AgCl}$ .  $\text{Cl} = 48.07$ .

$\text{C}_6\text{H}_5\text{N}_2\cdot \text{H}_2\text{SnCl}_6$  requires  $\text{Sn} = 26.88$ ;  $\text{Cl} = 48.18$  per cent.

No double haloids of *o*-phenylenediamine could be prepared.

*p-Phenylenediamine Stannochloride*,  $\text{C}_6\text{H}_5\text{N}_2\cdot \text{H}_2\text{SnCl}_4$ .—This salt was obtained as a mass of compact, opaque, white crystals readily soluble in water. The solution was easily hydrolysed by gently warming. The crystals melted and decomposed at  $270^\circ$ :

0.5547 gave 0.2246  $\text{SnO}_2$ .  $\text{Sn} = 31.90$ .

0.5547 „ 0.8436  $\text{AgCl}$ .  $\text{Cl} = 37.63$ .

$\text{C}_6\text{H}_5\text{N}_2\cdot \text{H}_2\text{SnCl}_4$  requires  $\text{Sn} = 32.06$ ;  $\text{Cl} = 38.26$  per cent.

*p-Phenylenediamine Stannichloride*,  $\text{C}_6\text{H}_5\text{N}_2\cdot \text{H}_2\text{SnCl}_6$ .—Oxidation of solutions of the stannochloride gave impure stannichloride. A pure specimen was obtained by treating *p*-nitroaniline with a molecular proportion of stannous chloride in hydrochloric acid. The nacreous plates dissolved in cold water without appreciable hydrolysis, but, on boiling, a precipitate was formed. The salt melted and decomposed at  $230^\circ$ :

0.3784 gave 0.1282  $\text{SnO}_2$ .  $\text{Sn} = 26.69$ .

0.1180 „ 0.2305  $\text{AgCl}$ .  $\text{Cl} = 48.32$ .

$\text{C}_6\text{H}_5\text{N}_2\cdot \text{H}_2\text{SnCl}_6$  requires  $\text{Sn} = 26.88$ ;  $\text{Cl} = 48.18$  per cent.

*Benzylamine Stannochloride*,  $\text{C}_6\text{H}_5\cdot \text{CH}_2\cdot \text{NH}_2\cdot \text{HSnCl}_3$ .—This salt was obtained by warming together benzonitrile (5 grams) and tin

(12 grams) in 50 c.c. of concentrated hydrochloric acid diluted with 20 c.c. of water under a reflux condenser for three hours. On cooling, a mass of short, silky crystals was deposited, which gave the usual reactions for stannochlorides, and softened at  $95^{\circ}$  and decomposed at about  $210^{\circ}$ :

0.4491 gave 0.2045  $\text{SnO}_2$ . Sn = 35.70.

0.2864 „ 0.3592  $\text{AgCl}$ . Cl = 31.03.

$\text{C}_7\text{H}_9\text{N}_2\text{HSnCl}_3$  requires Sn = 35.63; Cl = 31.93 per cent.

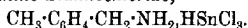
*Benzylamine Stannichloride*,  $(\text{C}_7\text{H}_9\text{N})_2\text{H}_2\text{SnCl}_6$ .—Benzonitrile (2.06 grams) was heated with stannous chloride (9.04 grams) in hydrochloric acid, with shaking, under a reflux condenser until a clear solution was obtained. From this, soft, shining crystals separated in flakes resembling naphthalene and melting at  $112^{\circ}$ :

0.3465 gave 0.0943  $\text{SnO}_2$ . Sn = 21.51.

0.3465 „ 0.5421  $\text{AgCl}$ . Cl = 38.83.

$(\text{C}_7\text{H}_9\text{N})_2\text{H}_2\text{SnCl}_6$  requires Sn = 21.85; Cl = 38.84 per cent.

*p-Methylbenzylamine Stannochloride*,



—Ten grams of tin and 5 grams of *p*-toluonitrile were heated with hydrochloric acid as in the case of the benzylamine salt, which this compound also resembled in properties. Both dissolved slowly in water, and the solutions soon decomposed. On heating, it melted at  $107^{\circ}$ :

0.5248 gave 0.2290  $\text{SnO}_2$ . Sn = 34.38.

$\text{C}_8\text{H}_{11}\text{N}_2\text{HSnCl}_3$  requires Sn = 34.29 per cent.

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## LXIV.—The Basic Carbonates of Copper.

By HORACE BARRATT DUNNICLIFF and SUDARSHAN LAL.

IN connexion with an investigation of the composition of a cellulose cuprammonium-hydroxide solution made by dissolving cotton-wool in a solution of commercial copper carbonate in ammonium hydroxide, one of the authors had occasion to examine a number of samples of commercial "copper carbonate."

Pickering (T., 1909, 95, 1410) states that the ordinary copper carbonate of commerce has the formula  $2\text{CuO}\cdot\text{CO}_2\cdot\text{H}_2\text{O}$ , identical

with malachite. The present paper does not support that statement.

According to some text-books, also, the compound precipitated when sodium carbonate is added to a solution of copper carbonate in the cold has the composition  $2\text{CuO} \cdot \text{CO}_2 \cdot 2\text{H}_2\text{O}$ , which changes to  $2\text{CuO} \cdot \text{CO}_2 \cdot \text{H}_2\text{O}$  on keeping.

The amount of copper oxide in thirteen different samples of commercial copper carbonate from different European and Indian sources is shown in table I. The percentages of copper oxide theoretically found in the basic carbonates of copper, for which a definite composition is claimed, are also quoted for purposes of comparison and reference.

TABLE I.

*Percentage of Copper Oxide found in Thirteen Samples of Commercial Copper Carbonate.*

1	2	3	4	5	6	7	8	9	10	11	12	13
78.80	71.71	71.52	69.69	69.58	69.55	69.29	68.90	68.61	68.41	68.36	67.84	66.16

Small quantities of impurity were present, usually iron, but in no case was the amount sufficient to account for the widely different results.

Name of Compound.	CuO per cent.	CO <sub>2</sub> per cent.	H <sub>2</sub> O per cent.
Pickering's compound ( <i>loc. cit.</i> ), $8\text{CuO} \cdot 3\text{CO}_2 \cdot 6\text{H}_2\text{O}$	... 72.62	15.06	12.32
Malachite, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ or $2\text{CuO} \cdot \text{CO}_2 \cdot \text{H}_2\text{O}$	... 71.94	19.95	8.11
Azurite, $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ or $3\text{CuO} \cdot 2\text{CO}_2 \cdot \text{H}_2\text{O}$	... 69.23	25.54	5.22
$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$ or $2\text{CuO} \cdot \text{CO}_2 \cdot 2\text{H}_2\text{O}$	... 66.53	18.41	15.06

Assuming that the commercial copper carbonates have the composition of malachite, it was thought that the adsorption of moisture on exposure to the atmosphere might account for the low results found. In order to test this, copper carbonate, in the form of a fine powder and spread in thin layers, was first dried in a steam-oven at  $97^\circ$  for more than three hours, and then, after weighing, was exposed to the atmosphere of the laboratory for three days ( $15$ — $17^\circ$ ) and weighed at intervals. The amount of increase in weight fluctuated during this time, but the maximum increase recorded amounted to 1.06 per cent. This would not account for the variations in copper oxide content shown in table I.

If the copper oxide content is any indication of the composition of the compound, it would appear that the commercial compound more nearly approximates to the composition of azurite. In order to obtain further evidence on this point, five samples were examined



which contained from 69.55 to 71.71 per cent. of copper oxide. The same samples contained from 17.35 to 18.1 per cent. of carbon dioxide. Comparison with the above table will show that these results are much below those required for malachite or azurite. It appears from this that the statement that commercial copper carbonate has the same composition as malachite is incorrect, and that in reality the substance is a mixture of very varying composition.

The authors of the present paper made various attempts to prepare a basic carbonate of copper of approximately constant composition in a simple manner, as it was desired to devise a process which could be used by comparatively inexperienced workers. Table II shows the methods employed and the percentages of copper oxide obtained.

TABLE II.

Method.	CuO per cent.
Copper sulphate solution precipitated in the cold with cold sodium carbonate solution ... ..	71.82
Copper sulphate solution (hot) precipitated with cold sodium carbonate solution ... ..	78.85
Copper sulphate solution (cold) precipitated with cold saturated solution of sodium hydrogen carbonate ... ..	77.09
Copper sulphate solution (cold) precipitated with cold 5 per cent. sodium hydrogen carbonate solution ... ..	71.08
Boiling saturated copper sulphate solution precipitated with cold saturated sodium hydrogen carbonate solution. The burner was removed before the addition of the sodium hydrogen carbonate ... ..	72.37

In all cases, the precipitates were washed free from sulphate.

These results yielded no valuable prospects, and it was decided to see if the desired result could be achieved by taking solutions of known strength. In the earlier experiments (from which tables I and II are compiled), the carbonates were carefully heated in a crucible, the residue being cooled in a desiccator and weighed. The heating, etc., was repeated until a constant weight was obtained. This method presents several defects, and it was decided to make complete analyses of the substances produced. This was done by heating a weighed amount of the substance in a boat contained in a short, lead-glass tube, the water and carbon dioxide being collected by means of the usual absorption apparatus employed in organic combustions. All heating was done by means of Bunsen burners manipulated by hand, and the experiment was carried out in an atmosphere of dry oxygen.

It was observed that in one or two cases the copper oxide was distinctly crystalline in appearance. In all the other cases, the

opper oxide was very dark brown, not black. Tests performed on the oxide showed it to be free from impurity.

A saturated solution of purified copper sulphate ( $14.5^{\circ}$ ) was diluted with an equal volume of distilled water, and to the cold solution was added a cold ( $14.5^{\circ}$ ) solution of pure sodium carbonate (10 per cent.). The precipitate was allowed to remain for twenty-four hours, and then washed on a Büchner funnel with distilled water until free from sulphate. The precipitate, on solution, contained no sulphate. It was dried in a steam-oven at  $96^{\circ}$  until its weight was constant.

TABLE III.

	CuO per cent.	CO <sub>2</sub> per cent.	H <sub>2</sub> O per cent.	Total per cent.
the average composition of the precipi- tate was ... ..	72.98	15.46	11.89	100.33
3CuO, 5CO <sub>2</sub> , 9H <sub>2</sub> O requires ... ..	73.02	15.54	11.44	100.00
Tinkering's compound 8CuO, 3CO <sub>2</sub> , 6H <sub>2</sub> O requires ... ..	72.62	15.06	12.32	100.00

The above percentages give the formula:  $13.07\text{CuO}, 5\text{CO}_2, 9.40\text{H}_2\text{O}$ .

The Basic Carbonate,  $2\text{CuCO}_3, 5\text{Cu}(\text{OH})_2$  or  $7\text{CuO}, 2\text{CO}_2, 5\text{H}_2\text{O}$ .

A solution of pure copper sulphate, saturated at  $14.5^{\circ}$ , was diluted with an equal quantity of distilled water, and to this solution was added a solution containing 5 per cent. of sodium carbonate and 5 per cent. of sodium hydrogen carbonate. The carbonate solution was added with stirring until, on filtering, a small portion, the filtrate gave no precipitate with it. The mixture was allowed to remain until next day, and was then filtered on a Büchner funnel and washed free from sulphate. This required

TABLE IV.

	CuO per cent.	CO <sub>2</sub> per. cent.	H <sub>2</sub> O per cent.	Total per cent.
1) Mean of three analyses ... ..	75.90	11.25	12.78	99.93
2) Mean of four analyses ... ..	75.48	11.55	13.18	100.21
3) Mean of three analyses ... ..	75.39	12.04	12.88	100.31
Mean ... ..	75.59	11.61	12.95	100.15
CuCO <sub>3</sub> , 5Cu(OH) <sub>2</sub> requires ... ..	75.77	11.98	12.25	100.00

Stated as formulæ the above results become:—

(a)  $7\text{CuO}, 1.89\text{CO}_2, 5.20\text{H}_2\text{O}$ .

(b)  $7\text{CuO}, 1.93\text{CO}_2, 5.39\text{H}_2\text{O}$ .

(c)  $7\text{CuO}, 2.01\text{CO}_2, 5.28\text{H}_2\text{O}$ .

Mean:  $7\text{CuO}, 1.94\text{CO}_2, 5.29\text{H}_2\text{O}$ .

Theory:  $7\text{CuO}, 2.00\text{CO}_2, 5.00\text{H}_2\text{O}$ .

many hours, and usually extended until the next morning. The wet precipitate was then allowed to remain until the third day and dried in a steam-oven. The drying process never lasted less than six hours.

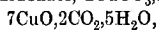
Three separate preparations, (a), (b), and (c), were made. The analyses of these preparations are shown in table IV (p. 721).

*Summary.*

Examination of a number of samples of commercial copper carbonate gave evidence to show that the statement that it has the same composition as malachite is erroneous.

An attempt has been made to prepare a basic copper carbonate of approximately constant composition from pure materials.

A new basic copper carbonate,  $2\text{CuCO}_3, 5\text{Cu}(\text{OH})_2$  or



is described.

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## Organic Chemistry.

**Nature of the Kolbe Electrochemical Synthesis of Hydrocarbons.** FR. FICHTER and EDUARD KRUMMENACHER (*Helvetica Chim. Acta*, 1918, 1, 146—166).—The authors discuss the two theories put forward to explain the mechanism of the Kolbe hydrocarbon synthesis, and draw the conclusion that the oxidation theory is more in accord with fact than the theory based on the ionic hypothesis. It is shown that peroxides are produced by electrochemical oxidation, on platinum anodes, of solutions of saturated fatty acids and their salts. Since these peroxides may be produced by the action of hydrogen peroxide on acid anhydrides, it is to be assumed that the separation of the anhydride is the first step in the hydrocarbon synthesis. The anhydride is then anodically oxidised, with the formation of a very unstable peroxide. The peroxide is then decomposed by the relatively high temperature of the anode, with the formation of the hydrocarbon, thus:  $R \cdot CO_2Na \rightarrow (RCO)_2O + O \rightarrow (RCO)_2O = O \rightarrow R \cdot R + 2CO_2$ , or a side reaction may also occur, thus:  $(R \cdot CO)_2O = O \rightarrow R \cdot CO_2 \cdot R + CO_2$ . When the peroxides are decomposed by heat, there is also a considerable amount of methane produced in addition to the expected hydrocarbon.

These considerations are adapted to the formation and decomposition of organic peracids. Organic peracids may be prepared by the action of hydrogen peroxide on both acids and anhydrides, consequently the formation of these substances electrolytically on the anode does not necessarily demand the intermediary formation of the anhydride. A further possibility also arises from the fact that peracids may be hydrolysed to peroxides. The peracids also decompose at the anode surface, giving carbon dioxide and an alcohol,  $R \cdot CO_3H \rightarrow R \cdot OH + CO_2$ , or carbon dioxide and an unsaturated hydrocarbon,  $C_nH_{2n+1} \cdot CO_3H = C_nH_{2n} + CO_2 + H_2O$ .

By the electrolysis of sulphonediadic acid or its salts, the products are carbon dioxide and sulphuric acid, and not the expected product, diethylene disulphone.

J. F. S.

**Determination of the Normal Density of Ethylene.** T. BATUECAS (*Anal. Fis. Quim.*, 1918, 16, 258—281; *Helvetica Chim. Acta*, 1918, 1, 136—141).—The mean of twenty-one determinations with samples of ethylene prepared from ethyl alcohol by phosphoric acid, boric acid, sulphuric acid, and alumina gave for the normal density the value  $L_0 = 1.26031$  grams.

A. J. W.

**Silver Acetylide.** JOHN EGGERT (*Zeitsch. Elektrochem.*, 1918, 24, 150—154. Compare A., 1918, ii, 228).—The amount of gaseous product produced by the detonation of silver acetylide depends on the method of preparation. Silver acetylide prepared

from an acid silver nitrate solution evolves about ten times the volume of gas, on detonation, as does material prepared in ammoniacal solution, neutral solution, or in solution of hydrofluoric acid. The material prepared in nitric acid solution contains 78.5% of silver, and the gaseous product of detonation consists of a mixture of carbon monoxide, carbon dioxide, methane, hydrogen, nitrogen, nitric oxide, and water vapour. The material prepared in 2% ammoniacal solution contains 89.5% of silver, and the product of detonation consists of carbon monoxide, carbon dioxide, methane, hydrogen, and water vapour. The analyses show that the product from nitric acid consists of 57% of silver acetylide and 43% of silver nitrate, whilst that from ammonia consists of 86% of silver acetylide and 14% of silver hydroxide. J. F. S.

**Methods of Formation of Chlorohydrins. I. Glyceryl Chlorohydrins.** L. SMITH (*Zeitsch. physikal. Chem.*, 1918, **92**, 717—740).

—The author has found that the velocity constants for the hydrolysis of chlorohydrins steadily decrease as the action proceeds and has attributed this action to the presence of two (or more) isomerides in the material employed. The nature of the chlorohydrin prepared by the various methods is not well investigated, and the usual methods are not very suitable for recognising these compounds in mixtures. The rate of hydrolysis by alkali hydroxides can be used for this purpose, and from the rate with which the velocity constant changes it is possible to state which isomerides are present. Using this method, the products obtained by the various methods for the preparation of glyceryl chlorohydrin have been examined. (1) Glyceryl monochlorohydrin, prepared from *epichlorohydrin*, consists entirely of  $\alpha$ -monochlorohydrin. (2) Monochlorohydrin from glycerol by the action of hydrogen chloride is a mixture of the  $\alpha$ - and  $\beta$ -compounds containing a large excess of the  $\alpha$ -derivative. (3) By the action of hypochlorous acid on allyl alcohol, a mixture of the  $\alpha$ - and  $\beta$ -chlorohydrins is produced which consists mainly of the  $\beta$ -compound. (4) The monochlorohydrin produced by the action of hydrogen chloride consists of a mixture of 85—90% of the  $\alpha$ -compound and 10—15% of the  $\beta$ -compound. A number of experiments are described which are designed to separate the constituents of the mixtures. (5) Glyceryl dichlorohydrin, prepared by the action of chlorine on allyl alcohol, contains only traces of the  $\alpha$ -compound. (6) The product of the action of hydrogen chloride on *epichlorohydrin* contains nothing but the pure  $\alpha$ -compound. (7) The product of the action of hypochlorite on allyl alcohol contains about one-third of its weight of  $\alpha$ -dichlorohydrin. The whole of the hydrolytic experiments were carried out with both baryta and sodium hydroxide.

J. F. S.

**Methods of Formation of Chlorohydrins. II. Propylene**

**Chlorohydrins.** LENNART SMITH (*Zeitsch. physikal. Chem.*, 1918, **93**, 59—88. See preceding abstract).—The author has prepared the propylene chlorohydrins by various methods, and has examined

the products by the kinetic method (*loc. cit.*) with the object of ascertaining their composition, and so deciding the best methods for preparing the different isomerides. (1) The product of the action of water on allyl chloride gives pure propylene  $\alpha$ -chlorohydrin; (2) by the action of sulphur chloride on propylene glycol, a product containing 25% of the  $\beta$ -compound and 75% of the  $\alpha$ -compound is obtained; (3) propylene glycol treated with hydrogen chloride yields more  $\beta$ -chlorohydrin than in case (2); (4) propylene oxide treated with hydrogen chloride yields mainly the  $\alpha$ -compound with not inconsiderable quantities of the  $\beta$ -compound; (5) the action of hypochlorite on propylene yields a mixture of the products. Henry's method (A., 1903, i, 725) for converting the  $\alpha$ -chlorohydrin into  $\beta$ -chlorohydrin has been examined, and it is shown that the product consists mainly of the  $\alpha$ -derivative.

J. F. S.

#### Autoxidation of some Derivatives of Thioncarbonic Acid.

O. BILLETER and B. WAVRE (*Helvetica Chim. Acta*, 1918, 1, 167—174).—Compounds containing the group  $\text{C}=\text{S}$ , and particularly those of the types  $\text{CS}(\text{OR})(\text{SR})$ ,  $\text{CS}(\text{OR})_2$ ,  $\text{CSCl}(\text{OR})$ , and thiocarbonyl chloride,  $\text{CSCl}_2$ , are phosphorescent and rapidly absorb oxygen, being thereby oxidised. These substances also emit a phosphorescent vapour. The oxidation occurs only in the presence of a catalyst such as a hydroxide of the alkali or alkaline earth metals, alkali carbonates, oxides of zinc or magnesium, and ammonia. Ethyl xanthate in the presence of excess of  $N/10$ -ammonia solution rapidly absorbs oxygen, and about 90% of the sulphur present is converted into sulphuric acid; some of the compound,  $\text{OEt}\cdot\text{CO}\cdot\text{SEt}$ , is also produced. Methyl methylxanthate in the presence of  $N$ -ammonia is oxidised very rapidly, the sulphur being oxidised to thiosulphate, sulphite, trithionate, and sulphate, whilst hexamethylenetetramine is also formed. Methyl thioncarbonate,  $\text{CS}(\text{OMe})_2$ , is rapidly oxidised, 38% of the sulphur being regained as sulphuric acid, whilst the rest appears as thio-sulphuric acid, sulphurous acid, and a little trithionic acid. The ethyl ester,  $\text{CS}(\text{OEt})_2$ , does not undergo autoxidation in the presence of pure oxygen, but with air 40% of the ester is oxidised and 14% of the sulphur appears as sulphuric acid, whilst the rest is obtained as thiosulphuric acid, sulphurous acid and a trace of trithionic acid. The chloro-ester,  $\text{CSCl}\cdot\text{OMe}$ , is oxidised so rapidly that in the first half minute 83% of the theoretical quantity of oxygen is absorbed, 16.9% of the sulphur is oxidised to sulphuric acid, and the residue to sulphurous acid. Thiocarbonyl chloride is very rapidly attacked, but only about 30% is oxidised normally, the residue being absorbed by the ammonia to form ammonium thiocyanate and sulphur.

J. F. S.

**Some Metallic Salts and Complex Metallic Derivatives of the Cyanocarboxylic Acids and their Esters. II.** LIZZIE PETERSON-BJÖRCK (*J. pr. Chem.*, 1918, [ii], 97, 51—58).—An

extension of the earlier paper (A., 1913, i, 27) giving a description of the cobalt and silver salts of cyanoacetic acid and of the platinum derivatives of methyl and ethyl cyanoacetate.

Cobalt cyanoacetate,  $(\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2)_2\text{Co}\cdot\text{H}_2\text{O}$ , obtained by the action of cyanoacetic acid on an aqueous suspension of cobalt hydroxide, forms pale red needles, the red aqueous solution of which becomes blue on warming. Silver cyanoacetate, prepared by precipitation from potassium cyanoacetate and silver nitrate in aqueous solution, forms colourless needles (compare Meves, *Annalen*, 1867, **143**, 304). By the interaction of barium cyanoacetate and chrome alum, it is possible to obtain green, prismatic crystals of a chromium cyanoacetate analogous to the ferric salt described earlier (*loc. cit.*). When agitated with an aqueous solution of potassium platinumochloride, the methyl and ethyl esters of cyanoacetic acid undergo conversion into the compounds  $\text{Pt}(\text{CO}_2\text{Me}\cdot\text{CH}_2\cdot\text{CN})\text{Cl}_2$  and  $\text{Pt}(\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CN})\text{Cl}_2$  respectively, each crystallising in needles. In the course of attempts to obtain platinum derivatives of free cyanoacetic acid, ammonia platinum sulphate,  $\text{Pt}(\text{NH}_3)_2\text{SO}_4$ , was treated with dilute aqueous cyanoacetic acid, a blackish-violet, crystalline compound being obtained of the composition  $(\text{NH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2)_2\text{Pt}$ .

D. F. T.

**Transformation of Methyl  $\alpha$ -Elæostearate into Methyl  $\beta$ -Elæostearate.** R. S. MORRELL (*J. Soc. Chem. Ind.*, 1918, **37**, 181—182r).—A continuation of the investigation of the properties of thickened drying oils (T., 1918, **113**, 111). The thickened "tung oil" was divided into fractions soluble and insoluble in acetone. The former was converted into the methyl ester by means of sodium methoxide, and this ester on hydrolysis yielded  $\beta$ -elæostearic acid; the same result was obtained from the fraction insoluble in acetone. The cerium salt was prepared from the undistilled ester, and since it was completely soluble in ether, it was evidently the salt of the  $\alpha$ -acid. The author concludes, therefore, that the stereoisomeric change occurs during the distillation of the ester.

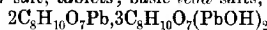
J. F. S.

**The Ethyl Hydrogen Citrates.** L. WOLFRUM and JOH. PINNOW (*J. pr. Chem.*, 1918, [ii], **97**, 23—50. See also A., 1915, ii, 679).—When esterified with ethyl alcohol in the absence of a catalyst, citric acid yields a mixture of *s*- and *ae*-ethyl dihydrogen and diethyl hydrogen citrates, of which the constitutions can be distinguished by colorimetric comparison of their ionisation constants (compare Palomaa, A., 1912, i, 6). The  $\alpha$ -hydroxy-acids predominate in the product, which also contains a small quantity of derivatives of aconitic acid. It is desirable to exclude moisture as completely as possible during the esterification. The constituent esters of the esterification product can be roughly separated by fractional extraction with ether in a Partheil-Rose apparatus, the final purification of the individual hydrogen esters being effected by recrystallisation of a suitable salt, the calcium salt of the

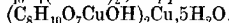
*as*-ethyl dihydrogen ester, the zinc salt of the *s*-ethyl dihydrogen ester, and the sodium salt of the *s*-diethyl hydrogen ester being selected for this purpose. As the *as*-diethyl hydrogen citrate is more soluble than its isomeride and has little tendency to the formation of crystalline salts, it is necessary to prepare this by an independent method from ethyl citrate; the partial alkaline hydrolysis of ethyl citrate yields only *as*-diethyl hydrogen citrate, and the further partial hydrolysis of this (or of ethyl citrate) yields *s*-ethyl dihydrogen citrate, so that a convenient method of preparation for each of these two esters is thus supplied (compare Pinnow, this vol., ii, 103; also Meyer, A., 1909, ii, 391, 803). The ester formed during the fermentation of citric acid is a mixture of the ethyl dihydrogen citrates.

*s*-Diethyl hydrogen citrate, needles, m. p. 58–59°, dissociation constant 1.514 at 15°, forms double molecules in ethereal solution; sodium salt, needles, m. p. 144–145°; *silver* salt, needles; *brucine* salt. The partition coefficient of this ester between ether and water was measured. The *as*-diethyl hydrogen citrate resembles the symmetrical isomeride in possessing a bitter taste, but with the exception of the silver salt, needles, m. p. 109.5–110.5°, the salts are amorphous.

*s*-Ethyl dihydrogen citrate, for which the partition coefficient between ether and water was determined, forms prisms, m. p. 97.5–98.5°; *silver* salt, tablets; basic *lead* salts,



and  $3\text{C}_8\text{H}_{10}\text{O}_7\cdot\text{Pb}\cdot\text{C}_8\text{H}_{10}\text{O}_7(\text{PbOH})_2$ ; *copper* salt,



greenish-blue prisms. *as*-Ethyl dihydrogen citrate gave a micro-crystalline, basic copper salt,  $(\text{C}_8\text{H}_{10}\text{O}_7\cdot\text{CuOH})_2\cdot\text{Cu}\cdot 2\text{H}_2\text{O}$ , and a zinc salt,  $2\text{C}_8\text{H}_{10}\text{O}_7\cdot\text{Zn}\cdot(\text{C}_8\text{H}_{10}\text{O}_7\cdot\text{ZnOH})_2\cdot\text{Zn}\cdot 13\text{H}_2\text{O}$ ; its brucine salt could not be resolved into enantiomorphous forms.

Ethyl citrate is generally contaminated by the presence of ethyl aconitate.

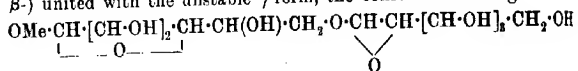
The earlier literature with respect to the ethyl hydrogen citrates is largely misleading and untrustworthy. D. F. T.

**Bromination in the  $\alpha$ -Position of the Aldehydes of the Fatty Series.** ANTONIO MADINAVEITIA and JOSÉ PUYAL (*Anal. Fis. Quim.*, 1918, 16, 329–337).—The chloro-ethers formed by the action of hydrogen chloride on mixtures of aldehydes and alcohols in equimolecular proportions are converted by bromine at 0° into chlorobromo-ethers, the bromine atom being adjacent to the chlorine. These derivatives are transformed by water into the  $\alpha$ -bromoaldehydes, and by alcohols into the corresponding bromo-acetals. The following compounds have been prepared:  $\alpha$ -chloro-9-bromodiethyl ether, b. p. 64–65°/13 mm.;  $\alpha$ -bromoacetal, b. p. 70–72°/20 mm.; methyl  $\alpha$ -chloro- $\beta$ -bromoethyl ether, b. p. 167°/decomp.; ethyl  $\alpha$ -chloro- $\beta$ -bromoisoamyl ether, b. p. 94–96°/15 mm.;  $\alpha$ -bromoisovaleraldehyde, b. p. 55–56°/25 mm.; and the corresponding diethyl acetal derivative,  $\text{CHMe}_2\cdot\text{CHBr}\cdot\text{CH}(\text{OEt})_2$ , b. p. 105–107°/30 mm. A. J. W.



**A New Form of Methylgalactoside and its Conversion into Octamethyldigalactose and into a Methylidigalactoside.**

MARY CUNNINGHAM (T., 1918, 113, 596—604).—The isolation of four galactose penta-acetates (Hudson, A., 1916, i, 546) indicates the possible existence of a modification of galactose analogous to  $\gamma$ -dextrose, and it is now shown that the syrupy form of methylgalactoside obtained from methyl alcohol and galactose at 100° in the presence of a little hydrogen chloride (Irvine and Cameron, T., 1905, 86, 907) is an ether of the  $\gamma$ -series. On methylation by the silver oxide method, the  $\gamma$ -methylgalactoside ( $[\alpha]_D + 12.95^\circ$  in alcohol,  $+25.9^\circ$  in water) is converted into tetramethyl  $\gamma$ -methylgalactoside identical with that described previously (Irvine and Cameron, *loc. cit.*), which on hydrolysis yields tetramethyl galactose; this substance at the ordinary temperature undergoes spontaneous polymerisation to octamethyl  $\gamma$ -digalactose,  $C_{20}H_{38}O_{11}$ . On heating methylgalactoside with acidic methyl alcohol, there is obtained an amorphous methylidigalactoside ( $[\alpha]_D$  in methyl alcohol,  $+85.6^\circ$ ; in water,  $+101.1^\circ$ ) identical with the substance regarded by Fischer (A., 1895, i, 439) as a methylgalactoside; the result is the same whether the original methylgalactoside is the  $\alpha$ -,  $\beta$ -, or  $\gamma$ -form, and it appears probable that in the presence of acidic methyl alcohol any one of these substances gives rise to an equilibrium mixture of all three, the unstable  $\gamma$ -modification then undergoing hydrolysis to give the reactive type of sugar; the product therefore consists of the stable forms of methylgalactoside ( $\alpha$ - and  $\beta$ -) united with the unstable  $\gamma$ -form, the constitution being



For experimental details, the original should be consulted.

D. F. T.

**Application of the Auto-condensation Powers of  $\gamma$ -Sugars to the Synthesis of Carbohydrate Complexes.**

MARY CUNNINGHAM (T., 1918, 113, 604—607. Compare preceding abstract).—From the observation that any one of the three methylgalactosides when heated with acidic methyl alcohol gives rise to a mixture of stereoisomeric condensation compounds consisting of the stable  $\alpha$ - and  $\beta$ -hexosides united with  $\gamma$ -galactose (preceding abstract), it is possible that similar compounds might be formed by merely dissolving a reducing sugar in this reagent and concentrating the solution. Experiment shows the correctness of this argument, but as the  $\gamma$ -sugar transiently produced may condense with preformed complexes, the products are often of greater complexity than methylidigalactoside (*loc. cit.*). Galactose and dextrose yield respectively a methyltetragalactoside and a methyltetraglucoside,  $C_{25}H_{44}O_{21}$ , whilst maltose gave a methyltrimaltoside,  $C_{37}H_{64}O_{31} \cdot H_2O$ . Towards Fehling's solution, the products behave as glucosides, whilst they also show the characteristic reactions of  $\gamma$ -compounds.

For experimental details, reference should be made to the original.  
D. F. T.

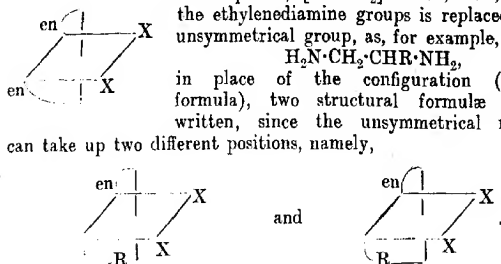
**The Degradation of Starch by Formaldehyde.** H. MAGGI and G. WOKER (*Ber.*, 1918, 51, 790—793. Compare A., 1917, i, 447, 686).—It has been shown that the dialysate obtained from a mixture of starch and formaldehyde has the properties of a solution of dextrin and simpler carbohydrates. A precipitate produced by adding alcohol to such a dialysate, redissolved in water, and allowed to become mouldy during the summer vacation, developed dextrose, identified as its osazone. Since the same mould produced dextrose from genuine dextrin, it is obvious that dextrin was present in the original dialysate, and since formic acid has no action on starch under the same conditions, the hydrolysis must be ascribed to the formaldehyde.  
J. C. W.

**Cellulose and Starch.** JEAN SARASIN (*Arch. Sci. phys. nat.*, 1918, [iv], 46, 5—32).—An inquiry into the constitution of cellulose and starch. A careful examination of the products of decomposition by heat of cellulose and starch indicates that in both cases *l*-glucosan is an intermediate product in the breaking-down process, and that this material itself when distilled under reduced pressure gives the same products as do starch and cellulose, in addition to the *l*-glucosan which they yield. Starch and cellulose are thus polymerides of *l*-glucosan, to which the author assigns the constitution (annexed formula), and he considers that it is the ring 2 which opens, giving two free valencies for the polymerisation, since amongst the products of decomposition of starch and cellulose 2:5-dimethylfuran is found.  
W. G.

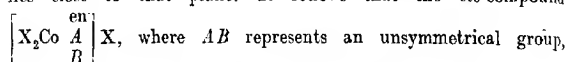
**Lignin. I. Lignosulphonic Acids.** M. HÖNIG and JACQUES SPITZER (*Monatsh.*, 1918, 39, 1—14. Compare Klason, A., 1908, i, 717).—The lignosulphonic acid obtained from different sulphite liquors varies considerably in composition (compare Seidel, *Mitt. k.k. Tech. Gewerbemuseums Wien.*, 1897, 7, 287) and consists of a mixture of substances. By fractional precipitation of the calcium or barium salts from aqueous solution by alcohol, it is possible to obtain fractions of distinct composition approximating, for the barium salts, to the formulæ  $C_{43}H_{60}O_{18}S_2Ba$ ,  $C_{40}H_{44}O_{18}S_2Ba$ , and  $C_{37}H_{44}O_{18}S_2Ba$ .  
D. F. T.

**A New Kind of Isomerism with Cobalt Compounds. Compounds containing Asymmetric Cobalt and Carbon.** A. WERNER (*Helvetica Chim. Acta*, 1918, 1, 5—32).—Among the three types of optically active cobaltamines which have been pre-

pared by Werner and his co-workers is the type represented by the *cis*-compound,  $[XCo en_2]X$ . If, now, one of the ethylenediamine groups is replaced by an unsymmetrical group, as, for example,  $H_2N \cdot CH_2 \cdot CHR \cdot NH_2$ , in place of the configuration (annexed formula), two structural formulæ can be written, since the unsymmetrical molecule can take up two different positions, namely,



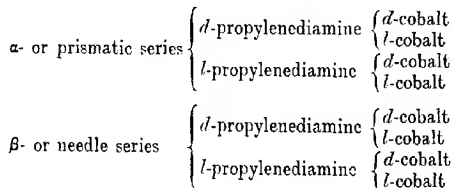
In the first formula the radicle R is far removed from the plane in which the two X-groups lie, whereas in the second formula it lies close to that plane. It follows that the *cis*-compound



should give two series of salts. If, for example,  $AB$  is propylenediamine (pn), there should be two series of *flavo*-salts, and this has actually been found to be the case. The two series are called the  $\alpha$ - and  $\beta$ -series, the former giving salts which crystallise in prisms and the latter salts which crystallise in needles.

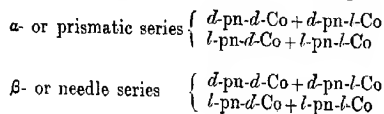
If, now, optically active propylenediamine is used, as well as optically active cobalt salt, further possibilities of the formation of isomerides occur. These possibilities, all of which have been realised experimentally, may be summarised as follows.

Eight optically active *flavo*-salts are possible, namely,



These optically active compounds can combine in different ways to give partly racemic compounds, which have also been prepared, namely:

(1) Four compounds which are racemic with respect to cobalt.



(2) Four compounds which are racemic with respect to propylenediamine.

$\alpha$ - or prismatic series  $\left\{ \begin{array}{l} d\text{-Co-}d\text{-pn} + d\text{-Co-}l\text{-pn} \\ l\text{-Co-}d\text{-pn} + l\text{-Co-}l\text{-pn} \end{array} \right.$

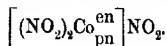
$\beta$ - or needle series  $\left\{ \begin{array}{l} d\text{-Co-}d\text{-pn} + d\text{-Co-}l\text{-pn} \\ l\text{-Co-}d\text{-pn} + l\text{-Co-}l\text{-pn} \end{array} \right.$

Further, by combination of the  $\alpha$ -salts of (1) and (2), and of the  $\beta$ -salts of (1) and (2), two completely racemic, and therefore inactive, compounds can be obtained.

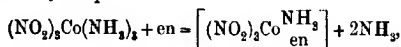
Also, using optically active propylenediamine, the *trans*-isomeride (*croceo*-salt) of the formula  $\left[ \text{X}_2\text{Co}_{\text{pn}}^{\text{en}} \right] \text{X}$  will give rise to three isomerides, namely:

$\left. \begin{array}{l} d\text{-trans-compound} \\ l\text{-trans-compound} \end{array} \right\} r\text{-trans-compound.}$

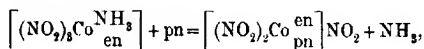
The compound used as the starting point in this investigation was dinitroethylenediaminepropylenediaminecobaltic nitrite,



To obtain this, trinitrotriamminecobalt,  $(\text{NO}_2)_3\text{Co}(\text{NH}_3)_3$ , was prepared by heating Erdmann's salt,  $[(\text{NH}_3)_2\text{Co}(\text{NO}_2)_4]\text{K}$ , with the molecular-equivalent quantity of ammonium nitrate. By the action of ethylenediamine in aqueous solution, the following reaction is made to take place:



giving trinitroammine-ethylenediaminecobalt. When this is further treated with the molecular equivalent of active propylenediamine, the following reaction occurs:



both *flavo*- and *croceo*-salts of dinitroethylenediaminepropylenediaminecobaltic nitrite being produced. By adding alcohol to the reaction mixture (in solution), the *flavo*-salts are precipitated, whilst the *croceo*-salts remain in solution and can be obtained by concentration. By heating the crude *flavo*-nitrites with water and sodium bromide the bromides can be obtained, and then transformed into the *d*-bromocamphorsulphonates, which are then resolved and separated by fractional crystallisation. From the pure, active bromocamphorsulphonates the active bromides can be obtained by treatment with hydrobromic acid. The fractional crystallisations involved are long and tedious, and for details the original paper must be consulted.

Resolution of the *flavo-d*-pn-salts gave rise to four pure *bromocamphorsulphonates*, which may be called *A*, *B*, *C*, and *D*. The

salts *A* and *B* belong to the prismatic series, and are optical antipodes with respect to cobalt, as was shown by a study of their bromides. They have respectively  $[\alpha]_D + 10^\circ$ ,  $[\alpha]_E + 100^\circ$ , and  $[\alpha]_D + 60^\circ$ ,  $[\alpha]_E + 30^\circ$ . The salts *C* and *D* belong to the needle series, and are also optical antipodes with respect to cobalt; their specific rotations are respectively  $[\alpha]_D + 20^\circ$ ,  $[\alpha]_E + 120^\circ$ , and  $[\alpha]_D + 0^\circ$ ,  $[\alpha]_E + 140^\circ$ .

Similarly, resolution of the *flavo-l-pn*-salts gave four pure *bromocamphorsulphonates*, *A*, *B*, *C*, and *D*. The prismatic salts *A* and *B* had  $[\alpha]_D + 106^\circ$ ,  $[\alpha]_E + 10^\circ$ , and  $[\alpha]_D + 62^\circ$ ,  $[\alpha]_E + 80^\circ$  respectively. The needle salts *C* and *D* had  $[\alpha]_D + 70^\circ$ ,  $[\alpha]_E + 92^\circ$ , and  $[\alpha]_D + 130^\circ$ ,  $[\alpha]_E + 14^\circ$  respectively. The pairs *A* and *B* and *C* and *D* were again optical antipodes with respect to cobalt.

The *flavo-dinitroethylenediaminepropylenediaminecobaltic bromides*,  $\text{XBr}$ , where  $\text{X} = \left[ (\text{NO}_2)_2\text{Co}^{\text{en}}_{\text{pn}} \right]$ , prepared from the above bromocamphorsulphonates, were all yellowish-brown in colour. *A* and *B* crystallising in prisms and *C* and *D* in needles. The specific rotations,  $[\alpha]_D$ , for the *d-pn*-series were:

	<i>d-Co.</i>	<i>l-Co.</i>
Prisms .....	$-30^\circ$ ( <i>B</i> )	$-60^\circ$ ( <i>A</i> )
Needles .....	$-6^\circ$ ( <i>C</i> )	$-108^\circ$ ( <i>D</i> )

The corresponding specific rotations for the *l-pn*-series were:

	<i>l-Co.</i>	<i>d-Co.</i>
Prisms .....	$+30^\circ$ ( <i>B</i> )	$+60^\circ$ ( <i>A</i> )
Needles .....	$+6^\circ$ ( <i>C</i> )	$+108^\circ$ ( <i>D</i> )

The *flavo-thiocyanates*,  $\text{XCNS}$ , were prepared from the bromides by treatment with sodium thiocyanate, and are yellow in colour. The specific rotations,  $[\alpha]_D$ , of the *d-pn*-series were: *A*,  $-64^\circ$ , *B*,  $-32^\circ$ , *C*,  $-6.5^\circ$ , *D*,  $-109^\circ$ , and of the *l-pn*-series: *A*,  $+64^\circ$ , *B*,  $+32^\circ$ , *C*,  $+6.5^\circ$ , *D*,  $+109^\circ$ .

The *flavo-sulphates*,  $\text{X}_2\text{SO}_4$  (the isomeride *A* crystallises with  $1\text{H}_2\text{O}$ ), were obtained from the bromides by reaction with ammonium sulphate. The specific rotations,  $[\alpha]_D$ , of the *d-pn*-series were: *A*,  $-63^\circ$ , *B*,  $-32^\circ$ , *C*,  $-7^\circ$ , *D*,  $-112^\circ$ , and of the *l-pn*-series, *A*,  $+63^\circ$ , *B*,  $+32^\circ$ , *C*,  $+7^\circ$ , *D*,  $+112^\circ$ .

The partly *racemic flavo-bromides*,  $\text{XBr}$ , were prepared synthetically by combining the proper constituents in pairs. The following compounds containing racemic cobalt and active propylenediamine were obtained. *d-pn-Series*: *A* + *B*,  $[\alpha]_D - 45^\circ$ ; *C* + *D*,  $[\alpha]_D - 57^\circ$ . *l-pn-Series*: *A* + *B*,  $[\alpha]_D + 45^\circ$ ; *C* + *D*,  $[\alpha]_D + 57^\circ$ . The compounds containing racemic propylenediamine and active cobalt were as follows: *d-pn-A* + *l-pn-B*,  $[\alpha]_D - 15^\circ$ ; *d-pn-B* + *l-pn-A*,  $[\alpha]_D + 15^\circ$ ; *d-pn-C* + *l-pn-D*,  $[\alpha]_D + 51^\circ$ ; *d-pn-D* + *l-pn-C*,  $[\alpha]_D - 51^\circ$ .

All the above *flavo*-salts show strong optical dispersion, and curves are given showing their rotations for fifteen wave-lengths between  $\mu\mu = 643.25$  and  $492$ .

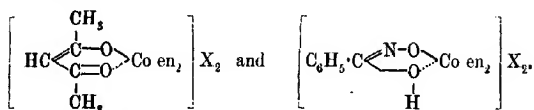
The completely *racemic flavo-salts* were prepared synthetically from the proper components, and were found to be inactive.

The *croceo-chlorides*,  $\text{XCl}$ , were prepared from the crude nitrites by treatment with cooled hydrochloric acid. They are golden-yellow in colour and less soluble than the bromides and iodides. The *d-pn-chloride* has  $[\alpha]_D -11^\circ$  and the *l-pn-chloride*  $[\alpha]_D +12^\circ$ .

The *d-pn-* and *l-pn-croceo-nitrites*,  $\text{XNO}_2$ , have  $[\alpha]_D \mp 22^\circ$ , and the corresponding *croceo-bromides*  $[\alpha]_D \mp 10^\circ$ . T. S. P.

#### Constitution of Internally Complex Metallic Salts. A

WERNER and SOPH. MATISSEN (*Helvetica Chim. Acta*, 1918, 1, 78–84).—Tschugaev has already shown that when dioximes are introduced into metal-ammonias, the dioximino-radicle occupies two co-ordination positions. In order to see if this holds in other cases, the authors have introduced acetylacetone and benzhydroxamic acid, which readily give internally complex salts, into cobalt-ammonias, and have found that these also occupy two co-ordination positions. The action of acetylacetone and benzhydroxamic acid respectively on hydroxo-aquodithylenediaminecobalt salts gives rise to acetylacetonato- and benzhydroxamato-diethylenediaminecobalt salts, which have the following general formulæ:



*Acetylacetonatodiethylenediaminecobalt bromide*,  $\text{YBr}_2 \cdot \text{H}_2\text{O}$ , where  $\text{Y} = [\text{C}_5\text{H}_7\text{O}_2\text{Co en}_2]$ , is prepared by heating a solution of 1 gram of hydroxo-aquodithylenediaminecobalt bromide in 10 c.c. of water with 0.6 gram of acetylacetone on the water-bath under reflux for half an hour, and then concentrating to half its volume. The bromide is precipitated by the addition of sodium or potassium bromide, and forms large, garnet-red crystals. By appropriate double decomposition of the bromide with other salts, as, for example, with potassium iodide to give the iodide, or with silver chloride to give the chloride, the following salts were prepared. The *iodide*,  $\text{YI}_2 \cdot \text{H}_2\text{O}$ , forms garnet-red prisms; the *chloride*,  $\text{YCl}_2 \cdot 2\text{H}_2\text{O}$ , gives dark red crystals; the *nitrate*,  $\text{Y}(\text{NO}_3)_3$ , crystallises in large, well-developed garnet-red crystals; the *sulphate*,  $\text{YSO}_4 \cdot 2\text{H}_2\text{O}$ , forms long, red needles; and the *perchlorate*,  $\text{Y}(\text{ClO}_4)_3$ , crystallises in large, ruby-red columns.

*Benzhydroxamatodiethylenediaminecobalt bromide*,  $\text{YBr}_2$ , where  $\text{Y} = [\text{C}_7\text{H}_9\text{O}_2\text{NCo en}_2]$ , is prepared by heating a solution of 1 gram of hydroxo-aquodithylenediaminecobalt bromide in 10 c.c. of water with the molecular-equivalent quantity of benzhydroxamic acid under reflux for half an hour. The solution is filtered from a light-coloured by-product and the bromide precipitated by the addition of sodium or potassium bromide. It forms large, almost black crystals with a metallic glance. The following salts were prepared from the bromide by methods similar to those mentioned for the acetylacetonato-salts. The *perchlorate*,  $\text{Y}(\text{ClO}_4)_3$ , forms large,

violet crystals possessing a metallic glance; the *dithionate*,  $\text{Y}_2\text{S}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$ , crystallises in fine needles; the *thiocyanate*,  $\text{Y}(\text{SCN})_3$ , gives dark violet, metallic-glistening octahedra; and the *sulphate*,  $\text{Y}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ , crystallises in rose-coloured, long, hair-like needles.

T. S. P.

**The Constitution of Carbamides. VI. Mechanism of the Synthesis of Urea from Urethane.** EMIL ALPHONSE WERNER (T., 1918, 113, 622—627).—Although the vapour density of urethane at  $203^\circ$  approximates to the theoretical, the ester gradually decomposes when boiled under reflux, yielding ethyl alcohol and cyanic acid, the latter being found as cyanuric acid.

The formation of urea from ammonia and urethane is therefore not a simple case of the conversion of an ester into an amide, but is actually a modification of Wöhler's synthesis, involving the union of ammonia and cyanic acid. Similarly, the decomposition of urethane by aqueous alkali is not a direct hydrolysis, as is commonly assumed, but actually occurs by the stages  $\text{OEt} \cdot \text{CO} \cdot \text{NH}_2 \rightarrow \text{OEt} \cdot \text{C}(\text{ONa}) \cdot \text{NH} \rightarrow \text{EtOH} + \text{NaOCN} \rightarrow \text{NaHCO}_3 + \text{NH}_3$ . On the other hand, when heated in a current of hydrogen chloride, urethane gives carbon dioxide, ethyl chloride, and alcohol, the acid therefore appearing to favour the constitution  $\text{OEt} \cdot \text{CO} \cdot \text{NH}_2$ , whereas alkali favours the constitution  $\text{OEt} \cdot \text{C}(\text{OH}) \cdot \text{NH}$ . When urethane is heated in aqueous solution at  $130^\circ$ , it gives rise to urea without the independent addition of ammonia, the cyanic acid arising from the dissociation of the urethane undergoing hydrolysis to urea. The relative difficulty of formation of urea from ethyl carbonate or carbamate and ammonia supports the view that urea does not contain two amino-groups, and the suggestion is made that two amino-groups, like two hydroxyl groups, cannot be attached stably to one carbon atom.

For experimental details, reference should be made to the original.

D. F. T.

**The Constitution of Dicyanodiamide.** WILLIAM J. HALL and FRANK C. VIBRANS (*J. Amer. Chem. Soc.*, 1918, 40, 1046—1063).—Of the many constitutions which have been proposed for dicyanodiamide, the authors' experiments favour the cyanoguanidine structure,  $\text{NH}_2 \cdot \text{C}(\text{NH}) \cdot \text{NH} \cdot \text{CN}$ , suggested by Bamberger in 1880. Pohl (A., 1908, i, 575) found that about one-half of the total nitrogen in the molecule is eliminated by sodium hypobromite, and, assuming that only an amino-group can react to this end, proposed the constitution  $\text{C}(\text{NH}_2)_2 \cdot \text{N} \cdot \text{CN}$ . The authors, however, using 20% sodium hypochlorite, have eliminated three-fourths of the nitrogen, the remaining atom being that in the cyano-group.

The quantity of nitrogen liberated by the reaction between dicyanodiamide and nitrous acid depends on the temperature and the concentration of the acid used as solvent. With 50% acetic acid as solvent, no nitrogen was evolved at the ordinary temperature, and at the b. p. only an amount corresponding with one-

quarter of an atom. With 85% acetic acid at the b. p. one atom of nitrogen was eliminated, with 95% acid two atoms, with glacial acetic acid about three atoms, whilst with 85% phosphoric acid all the nitrogen in dicyanodiamide was eliminated in the elementary state. Dicyanodiamide, therefore, undoubtedly contains one amino-group, as is evidenced by the comparative ease with which the first atomic proportion of nitrogen is eliminated. If a second amino-group were present, its interaction with nitrous acid should proceed under practically the same conditions. The development of a second amino-group in the course of the decomposition might therefore account for the higher temperature and longer time necessary for interaction with a second molecule of nitrous acid. The authors have failed to find a compound containing an amino-group which in 85% acetic acid at the b. p. does not react with nitrous acid; even guanidine, which, as stated by Van Slyke, fails to yield any nitrogen in 50% acetic acid at the ordinary temperature, yields two atomic proportions (but never more than two) in hot, more concentrated acetic acids. The fact that the condensation product of dicyanodiamide and formaldehyde, to which Pohl (*loc. cit.*) ascribes the constitution  $\text{OH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}(\text{NH}_2)\cdot\text{N}\cdot\text{CN}$  derived from his formula for dicyanodiamide, does not yield any nitrogen in 85% acetic acid suffices, therefore, to disprove Pohl's constitution, leaving for the condensation product the alternative constitution  $\text{OH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{CN}$  derived from the Bamberger formula for dicyanodiamide.

When an aqueous solution of dicyanodiamide and acetylacetone is boiled with a little 2*N*-sodium hydroxide, a substance,  $\text{C}_7\text{H}_7\text{N}_4$ , is obtained which does not contain a primary amino-group, but responds to the Liebermann and the Hinsberg tests for secondary amines. The formation of this substance disproves, according to the authors, Pohl's formula for dicyanodiamide, since they assert that this would lead to the formula of a condensation product containing neither primary nor secondary amino-groups. The substance  $\text{C}_7\text{H}_7\text{N}_4$  is regarded as 2-imino-1-cyano-4:6-dimethyl-1:2-dihydro-

pyrimidine,  $\text{NH}\cdot\text{C} \begin{smallmatrix} \text{N}=\text{CMe} \\ \text{N}(\text{CN})\cdot\text{CMe} \end{smallmatrix} \text{CH}$ . It forms colourless needles, m. p.  $225^\circ$ , yields a silver salt,  $\text{C}_7\text{H}_7\text{N}_4\text{Ag}$ , and is converted by boiling dilute sulphuric acid (1:5) into 2-imino-4:6-dimethyl-1:2-dihydropyrimidine,  $\text{C}_6\text{H}_6\text{N}_4\cdot\text{H}_2\text{O}$ , lemon-yellow prisms, m. p.  $199^\circ$  (decomp.; anhydrous), which yields the well-known acetylacetonecarbamide when boiled with 4*N*-sodium hydroxide.

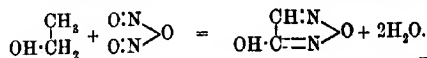
The condensation of dicyanodiamide (Bamberger's formula) and acetylacetone could yield a product which might be 2-imino-1-cyano-4:6-dimethyl-1:2-dihydropyrimidine (as stated above) or 2-cyanoamino-4:6-dimethylpyrimidine, but the latter alternative is excluded, because the product does not give Combes's aminodimethylpyrimidine on hydrolysis with boiling dilute sulphuric acid.

C. S.

**Mercury Fulminate.** W. R. HODGKINSON (*J. Soc. Chem. Ind.*, 1918, 37, 190r).—The author points out that mercury fulminate



cannot be formed in the absence of nitrous acid or a mixture of nitric oxide and nitrogen peroxide; he therefore represents the formation and constitution of fulminic acid by the equation:



J. F. S.

**The Decomposition of Solutions of Hydrocyanic Acid.** W. LEWCOCK (*Pharm. J.*, 1918, 101, 50—51).—The decomposition of solutions of hydrocyanic acid with the formation of a yellow or brown coloration or deposit is attributed to the action of small quantities of basic substances which are principally derived from the glass vessels, but might also be introduced by the use of hard water in preparing the solutions. A similar decomposition is observed in concentrated solutions of sodium cyanide on the addition of sodium carbonate, but not in presence of sodium hydroxide. In this case, it would appear that the alkali influences the hydrogen cyanide liberated by hydrolysis of the cyanide, whereas in presence of sodium hydroxide this hydrolysis is suppressed. Experiments showed that the addition of bases and salts with alkaline reaction greatly accelerated the decomposition of dilute solutions of hydrocyanic acid. The effect of bases derived from glass was studied by sealing up portions of an 8% solution of hydrocyanic acid with finely powdered glass, together with various substances which might be expected to retard the decomposition, and observing the length of time required for the appearance of a yellow coloration. The retardation was most marked in the presence of acids, and the addition of 1% of sulphuric acid, calculated on the weight of hydrocyanic acid, delayed the appearance of the colour for twenty-three days, as compared with two days in the case of the solution of hydrocyanic acid in distilled water. Tartaric acid equivalent to half the above quantity of sulphuric acid preserved the solution for twelve days, and saturation with carbon dioxide delayed decomposition for thirteen days. The preservative effect of various substances in the presence of glass would therefore appear to depend essentially on their acidity, and it was found that substances such as alcohol, glycerol, and mannitol were entirely without influence. With a higher concentration of tartaric acid (0.04 gram in 5 c.c.), the 8% solution of hydrocyanic acid remained unaffected in the presence of glass for more than four months, and it is concluded that 10% of sulphuric acid, on the weight of the hydrocyanic acid, would preserve the solution indefinitely.

J. F. B.

**Complex Uranyl Compounds.** ARNO MÜLLER (*Zeitsch. anorg. Chem.*, 1918, 103, 55—68).—A number of complex compounds of the uranyl radicle with cacodylic acid, *o*-, *m*-, and *p*-sulphaminobenzoic acids, toluene-*o*-sulphonic acid, and  $\alpha$ -phenylcinchoninic acid have been prepared. The cacodylic acid compound

is of special interest on account of its therapeutic properties. By treatment with hydrogen sulphide in alcoholic suspension, it is converted into a dithio-derivative.

*Uranyl cacodylate*,  $\text{UO}_2[\text{AsO}_2(\text{CH}_3)_2]_2$ , is prepared by double decomposition of sodium cacodylate and uranyl acetate. It forms a bright yellow, odourless, and tasteless powder, is decomposed by acids and alkalis, and when strongly heated evolves cacodyl vapours, leaving a residue of  $\text{U}_3\text{O}_8$ .

*Uranyl thiocacodylate*,  $\text{UO}_2[\text{AsOS}(\text{CH}_3)_2]_2$ , is difficult to isolate owing to its instability. By evaporating its alcoholic solution in a vacuum desiccator, it is obtained as a reddish-brown, crystalline mass with a mercaptan-like odour, m. p. 60–65°.

*Uranyl o-sulphaminobenzoate*,  $\text{UO}_2[\text{C}_6\text{H}_4(\text{SO}_2\text{NH}_2)\cdot\text{CO}_2]_2\cdot 3\text{H}_2\text{O}$ , forms small, greenish-yellow crystals with a metallic taste. *Uranyl m-sulphaminobenzoate* forms a dihydrate. *Uranyl p-sulphaminobenzoate* forms a monohydrate.

*Uranyl toluene-o-sulphonate*,  $\text{UO}_2[\text{C}_7\text{H}_7\cdot\text{SO}_3]_2\cdot 2\text{H}_2\text{O}$ , forms fairly large, bright yellow leaflets.

*Uranyl α-phenylcinchonate*,  $\text{UO}_2[\text{C}_6\text{NH}_5\text{Ph}\cdot\text{CO}_2]_2$ , is a dark yellow, tasteless and odourless amorphous powder. E. H. R.

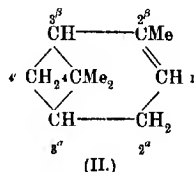
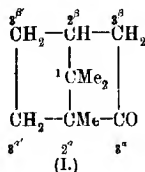
**Dissociation as a General Phenomenon with Hydrocarbons.** HANS MEYER and ALICE HOFMANN (*Monatsh.*, 1918, 39, 107–128).—The observed action of heat on organic substances, particularly hydrocarbons, indicates the occurrence of dissociation of hydrogen from carbon at a C–H-linking; the effect is not appreciable at the ordinary temperature, but becomes so when the dissociation process is favoured by rise of temperature, the influence of light, and of electrical or radioactive radiation. Substances which will remove one or other of the products of the dissociation should also extend its effect, and examples are quoted in which oxidation is already known to cause a condensation of two aromatic nuclei. The general evidence supplied by the nature of the constituents of coal tar supports the further view that in pyrogenic reactions long side-chains tend to become shortened, and this accords well with the fact that longer chains are more easily attacked, for example, by oxidising agents.

An examination of anthracene oil revealed the presence of diphenyl, together with a mixture of the ditolyls, but dibenzyl could not be detected. *iso*Propylbenzene when heated strongly decomposes mainly into toluene and trioxymethylene, the latter arising from the severed methylene groups. Methyl phthalate gives methyl benzoate, formaldehyde, and methyl diphenyltricarboxylate. Methyl acetate gives α-trioxymethylene as the main product, and no ethyl succinate. The action of sunlight on a suspension of ethyl dihydrolutidinedicarboxylate in benzene gives ethyl lutidinedicarboxylate. D. F. T.

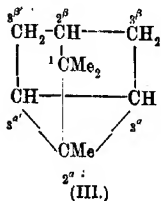
**Nomenclature of Singly- and Multiply-divided Carbon Rings. Bridge Linking.** J. BREDT and MARIA SAVELSBERG (*J. pr. Chem.*, 1918, [ii], 97, 1–22).—After reviewing the various

methods of nomenclature suggested hitherto for cyclic organic compounds containing bridged linkings and indicating their respective weaknesses, the authors suggest a scheme in which as far as possible the numbering of the carbon atoms is commenced at an atom possessing no symmetrical counterpart in the molecule, and, in the numbering, careful consideration is given to planes of symmetry in the molecule. The conception of a "bridge" is limited by the exclusion of molecules in which the bridge exists between two ortho-positions in a *cyclohexane* ring, such compounds, for example, decahydronaphthalene, being classified as containing condensed nuclei. With more complex cyclic molecules, the excessive use of numbers is avoided as far as possible by the use of names, so that each number represents a single position. The various cyclic systems as far as possible are referred to *cyclohexane*, and are grouped into (a) single rings, (b) double rings containing a meta- or para-bridge, or composed of rings condensed together by an amphi- or a spiro-attachment, and polycyclic compounds containing bridges together with a peri-linking, or consisting of combinations of (a) and (b).

The following examples illustrate this system of nomenclature. In the camphane and fenchane group, the molecule of camphor (annexed formula, I) may be taken as typical, the corresponding name being *p-mesomethylene-1:1:2-trimethylcyclohexan-3-one*. The atoms in compounds of the pinane group are distinguished by

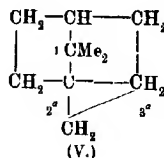
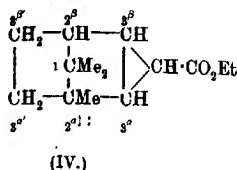


the method shown in formula II (annexed), which shows pinene to be *m-mesomethylene-4:4:2-trimethylcyclo-Δ<sup>1,2</sup>-hexene*. By the idea of a bridged ring as defined above, the carane group is excluded from the new system of nomenclature; its inclusion offers no great difficulty, but preference is given to the description of carane as *amphimethylenecyclohexane*. The carbon atoms in tricyclic



(*α-pericyclocamphane*) are numbered as in formula III (annexed), the corresponding name being *p-mesomethylene-1:1:2-trimethyl-3<sup>α</sup>-pericyclocyclohexane*, whilst as further examples may be mentioned Buchner's condensation product of ethyl diazoacetate and bornylene, which receives the name ethyl *p-mesomethylene-1:1:2-trimethylcyclohexane-amphi-3<sup>β</sup>-methylenecarboxylate* (formula IV), and the parent hydrocarbon of Forster's hydroxy-

camphene (formula V), which is described as *p*-mesonethylene-1:1-dimethylcyclohexane-*amphi*-2<sup>a</sup>:3<sup>a</sup>-methylene.



D. F. T.

### Nitrosotriphenylamine and Colours of the Second Order.

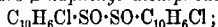
JEAN PICCARD and MORRIS KHARASCH [and, in part, E. H. FLECK] (*J. Amer. Chem. Soc.*, 1918, **40**, 1074—1079).—It is well known that the colour of a yellow dye is lowered by increase of molecular weight through orange, red, violet, blue, to green owing to a shift of its maximum absorption band towards the red end of the spectrum. Absorption colours have much in common with interference colours, and the first absorption band or group of bands is always followed by a second one, which is the octave of the first. When a dye with a lower colour than green is prepared, therefore, colours of the second order are obtained (Piccard, A., 1913, i, 895), but hitherto dyes giving more than a yellowish-green or greenish-yellow have not been prepared. The authors have now prepared an orange compound of the second order. A suspension of triphenylamine (prepared by heating diphenylamine and iodobenzene in nitrobenzene with an excess of potassium carbonate and a little catalytic copper at 207° for twelve hours) in absolute alcohol saturated with hydrogen chloride was slowly treated at -5° with amyl nitrite, dry hydrogen chloride being passed through the mixture. The crude, orange-red or carmine hydrochloride is suspended in cold water for two hours, the resulting crude base is collected, washed with cold water, dried in a vacuum desiccator, dissolved in dry ether, and the solution treated with hydrogen chloride, whereby *p*-nitrosotriphenylamine hydrochloride (*diphenylbenzoquinonemonoimine oxime chloride*),  $\text{OH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NPh}_2\text{Cl}$ , is obtained; it crystallises in long, brown needles, m. p. 178°. *p*-Nitrosotriphenylamine,  $\text{NO}\cdot\text{C}_6\text{H}_4\cdot\text{NPh}_2$ , obtained by hydrolysing the preceding hydrochloride with water, forms long, brown needles (orange when powdered), m. p. 120·5° (corr.), gives a yellow solution in benzene and an orange solution in alcohol, and yields Herz's *p*-acetylaminotriphenylamine by reduction with zinc and acetic acid, followed by acetylation. The colours of the base and its hydrochloride are alike, but that of the former is orange of the second order and that of the hydrochloride orange of the first order. C. S.

**Sulphur  $\beta$ -Naphthyl Chlorides.** [ $\beta$ -Chlorothiophthalenes.] TH. ZINCKE and K. EISMAYER (*Ber.*, 1918, **51**, 751—767. Compare A., 1912, i, 762; 1915, i, 234).—When  $\beta$ -thiophthalene

is treated with chlorine, it first suffers oxidation to the disulphide, then changes into the unstable  $\beta$ -chlorothiolenaphthalene, and finally yields 1-chloro- $\beta$ -chlorothiolenaphthalene. This is a comparatively stable substance, capable of taking part in many reactions, a number of which are described.

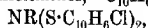
$\beta$ -Thiolenaphthalene is obtained by the reduction of crude naphthalene- $\beta$ -sulphonyl chloride with zinc dust in alcoholic solution.  $\beta$ -Chlorothiolenaphthalene, prepared by the action of chlorine (1 mol.) in dry chloroform, is a yellowish-red powder, m. p. 50–60°, which readily changes into di- $\beta$ -naphthyl disulphide on treatment with alkalis, alcohol, acetone, aniline, or  $\beta$ -naphthol, or when kept. 1-Chloro- $\beta$ -chlorothiolenaphthalene,  $C_{10}H_6Cl \cdot SCl$ , the product obtained by using twice the amount of chlorine, forms small, hard, yellowish-red crystals, m. p. 74–75°. This is oxidised by chlorine in glacial acetic acid solution to 1-chloronaphthalene- $\beta$ -sulphonyl chloride, m. p. 84–85° (compare Cleve, A., 1892, 345), the corresponding anilide having m. p. 171–172°.

Methyl 1-chloro- $\beta$ -naphthylsulphinite,  $C_{10}H_6Cl \cdot S \cdot OMe$ , an almost colourless, unstable oil, is prepared by the action of dry sodium methoxide on the chlorothioliol, but the corresponding acid is unknown. Attempts to isolate it, for example, by the action of *N*-sodium carbonate on the chlorothioliol, result in the formation of the anhydride, di-1-chloro- $\beta$ -naphthyl sulphoxide [di-1-chloro- $\beta$ -thiolenaphthyl oxide],  $O(S \cdot C_{10}H_6Cl)_2$ , which separates in pale yellow crystals, m. p. 149°. This is reconverted into the chlorothioliol by means of phosphorus pentachloride, whilst warm *N*-sodium hydroxide transforms it into di-1-chloro- $\beta$ -naphthyl disulphide,  $S_2(C_{10}H_6Cl)_2$ , thin, glistening leaflets, m. p. 141–142°, and 1-chloro- $\beta$ -naphthylsulphinic acid,  $C_{10}H_6Cl \cdot SO_2H$ , felted needles, m. p. 138–139° (methyl ester, from the silver salt, long needles, m. p. 139–140°). If the oxide is boiled with glacial acetic acid, it changes into di-1-chloro- $\beta$ -naphthyl disulphoxide,



this may also be prepared by the interaction of the chlorothioliol and the silver salt of the foregoing sulphinic acid, and it crystallises in colourless, prismatic needles, m. p. 152–153°, and liberates iodine from potassium iodide.

The chlorothioliol reacts with bases in indifferent solvents to form "thiolamines" and "dithiolamines,"  $C_{10}H_6Cl \cdot S \cdot NR_2$  and



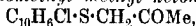
where  $R = H$  or a radicle. Thus, aqueous ammonia yields 1-chloro- $\beta$ -naphthylthiolamine, which crystallises in small, stout needles, m. p. 160° (becomes red at 95° and partly decomposes at 105–110°), and forms a benzylidene compound,  $C_{10}H_6Cl \cdot S \cdot N : CHPh$ , m. p. 106–107°. Ethereal ammonia produces di-1-chloro- $\beta$ -naphthylthiolimine as a pale pink powder, m. p. 213–214°, which may also be obtained by treating the amine with glacial acetic acid in the cold. Methylamine yields 1-chloro- $\beta$ -naphthylthiolmethylaniline, small leaflets, m. p. 89–90°, and the imine,  $NMe(S \cdot C_{10}H_6Cl)_2$ , m. p. 177–178°. 1-Chloro- $\beta$ -naphthylthiolanilide, prismatic

needles, m. p. 132°, *α*-naphthylidide, hard crystals, m. p. 154°, and *β*-naphthylidide, small needles, m. p. 132—133°, are prepared from the amines in benzene solution.

The naphthylamines behave differently if applied to the chlorothiol in warm glacial acetic acid solution. In these circumstances, the reaction resembles the coupling of a diazonium chloride with the bases. Thus, *α*-naphthylamine yields 2:4-di-1'-chloro-*β*-naphthylthio-*α*-naphthylamine [1-aminonaphthyl 2:4-di-1'-chloro-*β*-naphthyl disulphide],  $\text{NH}_2 \cdot \text{C}_{10}\text{H}_7 \cdot \text{S}(\text{C}_{10}\text{H}_6\text{Cl})_2$ , m. p. 85—87°, which forms an *acetyl* derivative, m. p. 144—145°, and a red azo-dye with *β*-naphthol, whilst *β*-naphthylamine gives 1-chloro-*β*-naphthyl 2-amino-*α*-naphthyl sulphide, in prisms and needles, m. p. 183—184°. The latter yields a *diacetyl* derivative, m. p. 153—154°, gives azo-dyes, and reacts with the original chlorothiol to form the compound,  $\text{C}_{10}\text{H}_6\text{Cl} \cdot \text{S} \cdot \text{NH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{S} \cdot \text{C}_{10}\text{H}_6\text{Cl}$ , m. p. 187—188°.

The chlorothiol also resembles a diazonium chloride in its reactions with tertiary aromatic amines and phenols, except that the components usually need to be heated to ensure success. Dimethylaniline yields *p*-dimethylaminophenyl 1-chloro-*β*-naphthyl sulphide,  $\text{C}_{10}\text{H}_6\text{Cl} \cdot \text{S} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$ , prisms and needles, m. p. 120—121°. *α*-Naphthol gives 1-chloro-*β*-naphthyl 4-hydroxy-*α*-naphthyl sulphide,  $\text{C}_{10}\text{H}_6\text{Cl} \cdot \text{S} \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH}$ , m. p. 116—118° (*acetate*, m. p. 138—139°); *β*-naphthol forms 1-chloro-*β*-naphthyl 2-hydroxy-*α*-naphthyl sulphide, large needles, m. p. 142—143° (*acetate*, m. p. 123—124°); and resorcinol yields *op*-dihydroxyphenyl 1-chloro-*β*-naphthyl sulphide, glistening leaflets, m. p. 153—154° (*diacetate*, m. p. 83—84°).

The chlorothiol also reacts with a number of ketones. For example, *acetone* gives 1-chloro-*β*-naphthyl *acetyl* sulphide (1-chloro-*β*-naphthylthiomethyl methyl ketone),

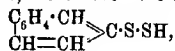


in colourless needles, m. p. 70—71°, which forms a *hydrazone*, glistening leaflets, m. p. 202°.

Potassium cyanide converts the chlorothiol into 1-chloro-*β*-naphthyl thiocyanate,  $\text{C}_{10}\text{H}_6\text{Cl} \cdot \text{SCN}$ , m. p. 118—119°.

J. C. W.

**Preparation of a New Type of Organic Sulphur Compound.** GERALD NOEL WHITE (I., 1918, 113, 608—609).—When *β*-naphthyl disulphide is heated with sodium sulphide crystals and sulphur, it gradually dissolves in the sodium polysulphide solution first formed. On cooling, glistening lamellae of sodium *β*-naphthylthiosulphoxylate separate, from which the free acid,



is liberated by dilute hydrochloric acid. The *lead* salt, obtained by double decomposition as an orange precipitate, on keeping gradually decomposes, the colour passing through scarlet to brown and black, whilst when heated with alcohol it yields *β*-naphthyl disulphide.

D. F. T.

**The Hydrindene-1:2-diols.** J. BÖESEKEN and CHR. VAN LOON (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 1186—1191).—The authors have repeated the work of Heusler and Schieffer (compare A., 1899, i, 365), and consider that they had obtained an impure *cis*-1:2-dihydroxyhydrindene, which is now found to have m. p. 107.5—108°. The diol described by Weissgerber (A., 1911, i, 623) is not really pure, but when obtained in the pure state from indene dibromide it is the *trans*-1:2-dihydroxyhydrindene, m. p. 159.8—160° (corr.). It gives a *diacetate*, b. p. 169—169.5°/13 mm. (corr.),  $D_4^{25}$  1.1771,  $n_D^{20}$  1.5170. The *cis*-*dibenzoate* has m. p. 109.5—110.5° (corr.), and the *trans*-*dibenzoate*, m. p. 76.5—77.5° (corr.), whilst the corresponding *phenylurethanes* have m. p. 205° (decomp.; corr.) and 206.5° (decomp.; corr.) respectively. A polymorphic modification of the *cis*-diol, m. p. 100.5—101.5° (corr.), obtained during the hydrolysis of the *cis*-*dibenzoate*, is described.

*Indene oxide*,  $\begin{matrix} \text{CH}_2 & \text{CH} \\ | & / \\ \text{C}_8\text{H}_7 & \text{CH} \end{matrix} > \text{O}$ , m. p. 31—31.5°, b. p. 113°/19.5 mm. (corr.),  $D_4^{25}$  1.1253,  $n_D^{20}$  1.5627, was obtained by the decomposition of bromohydroxyhydrindene by potassium hydroxide in ether. This oxide, as well as the *cis*- and *trans*-dihydroxyhydrindenes, readily gave  $\beta$ -hydrindone when warmed with dilute sulphuric acid. Indene oxide when carefully hydrated gave a mixture of the *cis*- and *trans*-glycols. W. G.

**Synthesis of Derivatives of Phenylethyl Alcohol.** JOSÉ RANEDO (*Anal. Fis. Quim.*, 1918, **16**, 351—354).—Magnesium benzyl chloride and chloromethyl ethyl ether,  $\text{CH}_3\text{Cl}\cdot\text{OEt}$ , react to form *phenylethyl ethyl ether*,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{OEt}$ , a liquid, b. p. 193—196°. Oxidation with chromic acid converts this substance into benzoic acid, and phosphorus pentachloride yields a liquid which decomposes when distilled at ordinary pressure into hydrogen chloride and a liquid, b. p. 200°. A. J. W.

**Sitosterol.** A. WINDAUS and ERIK RAHLÉN (*Zeitsch. physiol. Chem.*, 1918, **101**, 223—235).—In the presence of palladium, sitosterol in acetic acid solution is reduced by hydrogen at 100°, forming *sitostanol*,  $\text{C}_{27}\text{H}_{48}\text{O}$ , flat four- or six-sided plates from alcohol, m. p. 137°,  $[\alpha]_D^{25} + 27.9^\circ$ ; *acetate*, m. p. 132°. The new compound closely resembles cholestanol, and on oxidation with chromic acid yields *sitostanone*,  $\text{C}_{27}\text{H}_{46}\text{O}$ , plates from alcohol, m. p. 157°,  $[\alpha]_D^{25} + 45.7^\circ$ , and, with excess of chromic acid, *sitostandicarboxylic acid*,  $\text{C}_{27}\text{H}_{44}\text{O}_4$ , plates from acetic acid, m. p. 225—227°. Both the latter compounds are analogous to, but not identical with, the corresponding cholesterol derivatives, cholestanol, and cholestandicarboxylic acid. On distillation of a mixture of sitostandicarboxylic acid and acetic anhydride at 280° in a vacuum, carbon dioxide and water are evolved, and a cyclic *ketone* produced,  $\text{C}_{26}\text{H}_{44}\text{O}$ , well-formed hexagonal crystals from methyl alcohol, m. p. 112°. Reduction of sitostanone with zinc amalgam in boiling acetic

acid solution yields the hydrocarbon, *sitostan*,  $C_{27}H_{48}$ , m. p. 85—85.5°, which resembles cholestan (m. p. 80—81°), but is certainly not identical with it. The observed differences between these derivatives of sitosterol and the corresponding ones derived from cholesterol indicate that the general resemblance of the parent substances cannot be ascribed to the possession of a common structure with a difference in the position of the hydroxyl radicle, the double linking, or of both. The difference between sitosterol and cholesterol must therefore be structural or steric. H. W. B.

**Anodic Formation of Ester simultaneously with Nitrobenzene and *o*-Nitrophenol from the Mononitrobenzoic Acids.** C. SCHALL (*Zeitsch. Elektrochem.*, 1918, **24**, 154—157).—A mixture of potassium *o*-nitrobenzoate and the free acid in acetic anhydride solution has been subjected to electrolysis at the ordinary temperature. The anode products of the electrolysis were nitrobenzene, *o*-nitrophenol, and the *o*-nitrophenyl ester of *o*-nitrobenzoic acid. The yield of the products depends on the temperature. In concentrated aqueous solutions of potassium acetate and *o*-nitrobenzoate, the anode products are nitrobenzene, *o*-nitrophenol, and methyl *o*-nitrobenzoate. The formation of the nitrophenol is to be regarded as an anodic oxidation product, since this substance is produced by the action of persulphate on the *o*-nitrobenzoate. The formation of nitrobenzene, which is the analogue of methane in the acetate electrolysis, is stated to be due to the thermal decomposition of an intermediate compound of a peroxide nature. J. F. S.

**The Direct Conversion of Nitriles into Esters.** PAUL PFEIFFER (*Ber.*, 1918, **51**, 805).—With reference to Spiegel's communication (this vol., i, 216), the author points out that examples of the direct conversion of nitriles into esters were given in his work on stilbene-*o*-carboxylic acids some years ago (*A.*, 1911, i, 448), where he also directed attention to the steric hindrance of a methyl group in the *ortho*-position. J. C. W.

**Direct Preparation of Aromatic Nitriles by Catalysis.** ALPH. MAILHE (*Bull. Soc. chim.*, 1918, [iv], **23**, 235—238).—Aromatic nitriles may be readily prepared with good yield by passing the vapours of the esters of the corresponding acids along with ammonia over aluminium or thorium oxides at 470—480°. This method has been successfully used with the methyl, ethyl, propyl, or *iso*amyl esters of benzoic, the three toluic, phenylacetic, and  $\alpha$ - and  $\beta$ -naphthoic acids. W. G.

**The Nature of Subsidiary Valencies. XVIII. Octamines. Influence of the Volume of the Anion.** FRITZ EPHEAUM [with E. ROSENBERG] (*Ber.*, 1918, **51**, 644—669. Compare this vol., ii, 115).—In the course of this work it has often been demonstrated that the ability of a substance to form additive compounds is intimately connected with the magnitude of the space



occupied by the various parts of the molecule. It is now shown that when the anion is particularly large, the additive capacity of the cation for negative substances becomes much more than it is normally. For example, very few cases of metallic ammines are known in which the number of molecules of ammonia is more than six, but several are now described, being salts of bivalent metals with aromatic acids, in which the number is eight. In explaining this, the author offers a picture of the arrangement of the metallic atoms within the crystal, each one surrounded by eight acid radicles; the larger these radicles are, the more room will there be for ammonia molecules around the metallic atom. He refers, in this connexion, to the remarkable fact that polyhydrates of some salts can combine with several molecules of hexamethylene-tetramine, and, conversely, compounds of salts with hexamethylene-tetramine or caffeine can combine with more water molecules than the salts alone (see A., 1911, i, 184, 266; 1912, i, 812).

That the chemical nature of the anion is not the factor which confers this extra additive capacity on the salt is proved by the fact that the corresponding alkali salts have no affinity for ammonia, and that carboxylates and sulphonates alike give rise to octammines. Additional evidence that the controlling factor is a spatial one is adduced from the fact that salts of dibasic acids, like phthalic and naphthalic acids, do not form octammines, whereas benzoates do.

Even in the aromatic series, however, the experimental material is by no means plentiful, for it so frequently happens that internal complexes are formed between some substituent in the acid and the metallic atom. For example, anomalous results, recognisable by unexpected colours and solubilities of the products, are often met with among halogeno-, amino-, and even ketonic acids.

An unusual phenomenon has been observed in some cases, for example, that of cobalt benzoate octammine, namely, that when once obtained, the ammines are stable at temperatures much above that at which alone they can be produced.

In the following list of hydrates and ammines, the temperatures given in brackets are those at which the vapour pressures are 760 mm., that is, they are the "dissociation temperatures" on which the author bases his comparisons of stability.

*Benzoates*.—Nickel; *hexahydrate*, pale green leaflets; *octammine* ( $-1.5^{\circ}$ ). Cobalt; *tetrahydrate*, grey with a tinge of pink, changes to the bluish-violet anhydrous salt at  $115^{\circ}$ ; *octammine* ( $32.5^{\circ}$ , but can only be prepared at about  $-20^{\circ}$ ). Copper; the peacock-blue anhydrous salt becomes first violet, then copper-coloured, then dark blue, further greenish-blue and green, and finally forms the grey *octammine* ( $-5.5^{\circ}$ ); the tensions of the blue *hexammine* ( $14^{\circ}$ ), red *tetrammine* ( $82.5^{\circ}$ ), and violet *diammine* ( $183^{\circ}$ ), are given in place of incorrect data quoted earlier (A., 1916, ii, 104). Manganese; *dihydrate*, very pale pink; *octammine* ( $10.5^{\circ}$ ). Zinc; *diammine* ( $190^{\circ}$ ), *tetrammine* ( $57^{\circ}$ ), *hexammine* ( $18^{\circ}$ ), *octammine* ( $-2.5^{\circ}$ ). Cadmium; *diammine* ( $182^{\circ}$ ), *tetrammine* ( $42^{\circ}$ ), *hex-*

*amine* (17.5°), *octamine* (6°). Ferrous; *trihydrate*, groups of pale green prisms; *octamine* (7°).

*Benzenesulphonates*.—Nickel; *hexahydrate*, microscopic, rhombic leaflets; *hexamine* (145.5°), bluish-violet. Copper; *hexahydrate*, very pale greenish-blue, silky; *pentamine*, small-blue. Zinc; *hexahydrate*, microscopic, rhombic leaflets; *tetramine* and *pentamine*.

*Sulphanilates*.—The copper salt is very sparingly soluble, olive-brown when cold, dark brown at 100°, and forms *penta-* and *hexamines* (blue). Nickel; *tetrahydrate*, pale bluish-green prisms; *hexamine* and *octamine* (below 0°), both pale reddish-violet.

*Phthalates*.—The pale blue copper salt forms a *hexamine*. Nickel; *dihydrate*, brilliant green; *hexamine*.

*Trinitrobenzoates*.—Copper; *dihydrate*; reddish-brown amines and an almost black *decamine* (the abnormal additive capacity is partly due to the participation of the nitro-groups).

*o-Naphthoylbenzoates*.—Nickel; *decahydrate*, very pale pink, not green, as most nickel salts; *hexamine* and *octamine* (15°). Copper; *tetra-* and *hexa-hydrates*, almost white; *octamine* (2°). Zinc; *octamine* (−6°).

*Naphthalates*.—Copper; *tetrahydrate*, slender, pale blue needles; *hexamine* (about 0°) and *tetramine*, both pale slate-grey. Zinc; *tetramine*.

*α-Naphthalenesulphonates*.—Nickel; *trihydrate*, very pale green; *tetra-* and *hexa-ammines*. Copper; *trihydrate*, almost snow-white, although the solution is deep green and the anhydrous salt pale yellowish-brown; *di-* and *tri-ammines*.

*β-Naphthalenesulphonates*.—Nickel; *nonahydrate*, green; *hexamine*, white; *octamine* (26°), very pale violet. Cobalt; *hexahydrate*, almost colourless; *octamine* (18.5°). Copper; *hexahydrate*, blue; *hexamine* (79.5°); *octamine* (−1°). Zinc; *hexahydrate*, silky leaflets; *octamine* (1.5°). Cadmium; *hexahydrate*; *hexamine* (90.5°). Ferrous; *hexahydrate*, leaflets; *octamine* (−10°). Manganese; *hexahydrate*, almost colourless; *octamine* (3.5°).

*Dibromonaphthalene-β-sulphonates*.—These are usually so very sparingly soluble that the acid might find application in analysis. Nickel, pearl-grey, forms a *hexamine* (above 150°) and *octamine* (0°). Copper, reddish-violet, forms a *tetramine*.

*Nitroprussides*.—Zinc; *trihydrate*; *tetramine* and *octamine* (−5°).

J. C. W.

**Hydrogenation of Aromatic Compounds by the Help of Platinum. III. Hydrogenation with Platinum containing Oxygen.** RICHARD WILLSTÄTTER and DANIEL JAQUET (*Ber.*, 1918, 51, 767–779).—As the application of platinum in the catalytic hydrogenation of organic compounds has developed, various authors have found that it sometimes makes a difference whether the metal is entirely free from oxygen at the commencement of a reduction or has been freely exposed to the air. In many cases, no difference

can be observed, for example, in the reduction of benzene by platinum black (A., 1912, i, 545), but Hess has found that the careful exclusion of oxygen is of great importance in the hydrogenation of pyrrole and certain derivatives (A., 1913, i, 1378). The present paper describes cases of the opposite nature, in which the metal needs to be "primed" occasionally with oxygen, and the conclusion is drawn that platinum itself and platinum loaded with oxygen are distinct catalysts.

A similar difference was observed by Purgotti and Zanichelli (A., 1904, ii, 329), who found that platinum free from air would not induce the decomposition of hydrazine, whilst ordinary platinum preparations will do so, but would cause the decomposition of hydrogen peroxide and hydroxylamine. The particular case now dealt with, however, is the hydrogenation of the anhydrides of *o*-dicarboxylic acids. For example, phthalic anhydride suffers practically no reduction in glacial acetic acid unless the apparatus is opened as occasion requires and the platinum-black is shaken with the air, when the reduction proceeds from stage to stage quite smoothly, the final products being hexahydrophthalide (mixed with a little *o*-hydroxymethylhexahydrobenzoic acid), hexahydro-*o*-toluic acid (a mixture of *cis*- and *trans*-isomerides), and hexahydrophthalic acid. The initial products include phthalide and *o*-toluic acid, which indicates that the anhydride ring is more readily attacked than the benzene nucleus, but in the case of phthalimide, which can only be hydrogenated in glacial acetic acid solution with the best spongy platinum (not necessarily activated by oxygen), the

sole product is hexahydrophthalimide, 
$$\begin{array}{c} \text{CH}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CO} \\ \text{CH}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CO} \end{array} \text{NH}$$
 monoclinic prisms, m. p. 132°.

Naphthalic anhydride also can only be hydrogenated by platinum which is activated from time to time by oxygen. The products include a tetra- and a deca-hydronaphthalide, decahydroacenaphthene,  $\text{C}_{12}\text{H}_{20}$ , and a tetrahydro-1-methylnaphthalene-8-carboxylic acid, needles, m. p. 150°.

The influence of such anhydrides on the reduction of the corresponding acids, and even benzene, is remarkable. Unless the precaution of activating the catalyst with oxygen is taken, hydrogenations that would otherwise proceed smoothly are inhibited by traces of these anhydrides. Thus, if phthalic acid is quite free from its anhydride, and naphthalic acid is freshly precipitated from an alkaline solution, they may be reduced to hexa- and tetrahydro-derivatives, respectively, under ordinary conditions, but not otherwise. *iso*Phthalic acid usually contains traces of phthalic anhydride, which inhibits reduction, but may be reduced to a mixture of *cis*- and *trans*-hexahydro-acids if pure and suspended in glacial acetic acid. *p*-Toluic acid readily yields *cis*- and *trans*-hexahydro-acids.

Indole is readily reduced in glacial acetic acid, the final product being perhydroindole (octahydroindole), which is an alkaline oil with an unpleasant odour, b. p. 182–183°/720 mm., 65°/

12 mm.,  $D_4^{20}$  0.9947, and forms a *platinichloride*, m. p. 172—173°, and a *picrate*, m. p. 137—138°. Partial hydrogenation gives a mixture of indole with di- and per-hydroindoles. The perhydro-indole may be extracted by shaking the ethereal solution with 0.1*N*-hydrochloric acid, and the other products separated by fractional precipitation with ethereal picric acid. The yellow *picrate* of the dihydro-base is formed first, and then the red salt of indole itself, and the change in colour is quite distinct at the point of contact of the two liquids. J. C. W.

#### Acetylaminophenyl Salicylate. Preparation of Salophen.

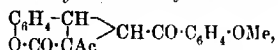
R. Q. BREWSTER (*J. Amer. Chem. Soc.*, 1918, **40**, 1136—1138).—An investigation of the causes of the poor yields obtained in the preparation of salophen. The reduction of the crude *p*-nitrophenyl salicylate must be effected in non-aqueous solution to prevent hydrolysis of the ester and its reduction product; with glacial acetic acid and zinc dust, the yield of *p*-aminophenyl salicylate is 45% of the theoretical. When this is acetylated without being isolated, the yield of crude salophen, m. p. 175—180°, is 60% of the theoretical.

Using purified *p*-nitrophenyl salicylate, the yield of *p*-aminophenyl salicylate is increased to 73%, and that of salophen to 80%, of the theoretical. [See *J. Soc. Chem. Ind.*, 1918, 530A.]

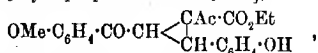
C. S.

**A New Group of cycloPropane Derivatives. II. Action of some Analogues of Phenacyl Haloids on 3-Acylcoumarins.** OSKAR WIDMAN (*Ber.*, 1918, **51**, 907—911. Compare this vol., i, 347).—The reaction described in the first paper is found to be common to other aryl halogenomethyl ketones.

Thus, *p*-chloroacetylanisole (*p*-methoxyphenyl chloromethyl ketone) reacts with 3-acetylcoumarin in the presence of sodium ethoxide to form 3-acetyl-3:4-anisacylidene coumarin,



which crystallises in long needles, m. p. 163°, and *ethyl α-acetyl-αβ-anisacylidene coumarinate* [*ethyl 1-acetyl-2-p-methoxybenzoyl-3-o-hydroxyphenylcyclopropane-1-carboxylate*],

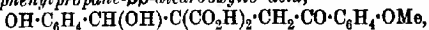


which separates from benzene in long, flat prisms with  $1\text{C}_6\text{H}_6$ , m. p. 70°, or 119—120° when free from solvent benzene.

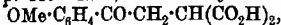
3-Benzoylcoumarin yields 3-benzoyl-3:4-anisacylidene coumarin, long, pointed prisms, m. p. 190°, whilst ethyl coumarin-3-carboxylate forms *ethyl 3:4-anisacylidene coumarin-3-carboxylate*, prisms, m. p. 165—166°, and *ethyl 2-p-methoxybenzoyl-3-o-hydroxyphenylcyclopropane-1:1-dicarboxylate*, m. p. 99—100°.

The ethyl 3:4-anisacylidene coumarin-3-carboxylate is hydrolysed

by 4% sodium hydroxide to *α*-hydroxy-γ-p-methoxybenzoyl-*α*-o-hydroxyphenylpropane-ββ-dicarboxylic acid,



short prisms, m. p. 119–120°, and *anisacetylmalononic acid*,



which crystallises in stellate groups of needles, m. p. 162° (decomp.), and may be synthesised by condensing *p*-chloroacetylanisole with ethyl sodiomalonate.

*o*-Chloroacetylanisole yields 3-acetyl-3:4-*o*-methoxyphenacylidene-coumarin, prisms, m. p. 144–145°; *ω*-bromo-*m*-nitroacetophenone gives rise to ethyl 3:4-*m*-nitrophenacylidene-coumarin-3-carboxylate, prisms, m. p. 162–163°, and ethyl 2-*m*-nitrobenzoyl-3-*o*-hydroxyphenylcyclopropane-1:1-dicarboxylate, large, hard crystals, m. p. 132–133°; and 1-chloroacetylnaphthalene (*α*-naphthyl chloromethyl ketone, b. p. 204–205°/18 mm.) produces 3-acetyl-3:4-*naphthacylidene*-coumarin, hard prisms, m. p. 133–134°.

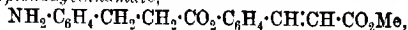
J. C. W.

### Some New Derivatives of *p*-Coumaric and Vanillic Acids.

FRITZ VON KONEK and EUGEN PACSU (*Ber.*, 1918, **51**, 855–865).—Some years ago, Konek synthesised methyl 3-amino-6-benzoyloxybenzoate hydrochloride and found that it had a cocaine-like effect (*Math. Naturwiss. Anz. Akad. Wiss., Budapest*, **14**, 16). The synthesis has now been extended to other phenolic acids in order to test the influence of the kind and position of the various groups on the physiological activity.

*p*-Coumaric (*p*-hydroxycinnamic) acid, from *p*-hydroxybenzaldehyde by Perkin's method, is converted into the methyl ester, and this is treated with *p*-nitrobenzoyl chloride and sodium hydroxide solution. The methyl *p*-4'-nitrobenzoyloxy-cinnamate, rosettes of silky, white needles, m. p. 203°, is reduced by means of tin and alcoholic hydrogen chloride to methyl *p*-4'-aminobenzoyloxy-cinnamate,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{Me}$ , which has m. p. 168–169°, and forms a very sparingly soluble hydrochloride, long needles, decomp. 215°, and sulphate.

For the preparation of another ester, β-*p*-nitrophenylpropionic acid was required. This is prepared as follows: β-phenylpropionic acid (hydrocinnamic acid) is dissolved in about ten times its weight of fuming nitric acid at 85°, the solution is poured into ice-water, and the crude product dissolved in about fifty times its weight of boiling water and then cooled to 65°, whereby the *p*-nitro-acid separates almost pure, leaving the *o*-nitro-acid to crystallise on cooling further. About 63% of the parent acid is converted into the para-derivative and 30% into the ortho-compound by this means. The desired acid is treated with thionyl chloride, and the β-*p*-nitrophenylpropionyl chloride, b. p. 189–192°/16 mm., m. p. 34–35°, is treated with methyl *p*-hydroxycinnamate, whereby methyl *p*-β-4'-nitrophenylpropionoxycinnamate is formed, in white needles, m. p. 131–132°. This is reduced to methyl *p*-β-4'-amino-phenylpropionoxycinnamate,



which crystallises in long needles, m. p. 153—154°, and forms a sparingly soluble *hydrochloride*, decomp. 250°.

5-Nitrovanillic acid (Vogl, A., 1899, i, 697) is converted by means of thionyl chloride into the chloride, 5-nitro-4-hydroxy-3-methoxybenzoyl chloride, m. p. 93—94°, this into the methyl ester, pale yellow, glistening needles, m. p. 148—149°, and then into methyl 5-nitro-4-benzoyloxy-3-methoxybenzoate, pale yellowish-brown needles, m. p. 124—125°, by means of benzoyl chloride and pyridine. This ester is reduced to methyl 5-amino-4-benzoyloxy-3-methoxybenzoate,  $\text{OBz}\cdot\text{C}_6\text{H}_2(\text{NH}_2)(\text{OMe})\cdot\text{CO}_2\text{Me}$ , which crystallises in needles, m. p. 188—190°, and forms a sparingly soluble *hydrochloride*, decomp. 236—240°.

Neither of the above amino-acid esters has any effect on the epidermis or tongue.

J. C. W.

**Some Piperilyhydrazones.** ALBERT WEINHAGEN (T., 1918, 113, 585—587).—A description of the condensation products of several aldehydes and ketones with piperilyhydrazine, the latter being obtained by the reduction of nitrosopiperidine.

Piperonalpiperilyhydrazone,  $\text{C}_{13}\text{H}_{16}\text{O}_2\text{N}_2$ , forms colourless needles, m. p. 65—67°; salicylaldehydepiperilyhydrazone,  $\text{C}_{12}\text{H}_{16}\text{ON}_2$ , needles, rhombic plates, or octahedra, m. p. 71—72°; formaldehydepiperilyhydrazone,  $\text{C}_8\text{H}_{12}\text{N}_2$ , prismatic needles, m. p. 78—79°; benzaldehydepiperilyhydrazone, pentagonal or hexagonal plates, m. p. 68—69° (compare Forster, T., 1915, 107, 267); anisaldehydepiperilyhydrazone,  $\text{C}_{12}\text{H}_{18}\text{ON}_2$ , hexagonal plates, m. p. 54°; p-hydroxybenzaldehydepiperilyhydrazone,  $\text{C}_{12}\text{H}_{16}\text{ON}_2$ , m. p. 161°; p-aminoacetophenonepiperilyhydrazone,  $\text{C}_{13}\text{H}_{19}\text{N}_3\cdot\text{H}_2\text{O}$ , prismatic crystals, m. p. 108°. With isovaleraldehyde, a small quantity of a substance, m. p. near 122°, was obtained, whilst with propionaldehyde, acetone, p-aminobenzaldehyde, dextrose, galactose, and l-xylose the products were resinous.

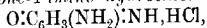
D. F. T.

**Attempt to Synthesise Fisetol.** J. TAMBOR and EDMOND M. DU BOIS (Ber., 1918, 51, 748—751).—*m*-Dimethoxybenzene is condensed with bromoacetyl bromide under the influence of aluminium chloride, and thus converted into 2-hydroxy-4-methoxyphenyl bromomethyl ketone (*o*-bromoresacetophenone methyl ether),  $\text{OH}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CO}\cdot\text{CH}_2\text{Br}$ , which crystallises in stout prisms, m. p. 92° (compare A., 1905, i, 916, and Auwers and Pohl, A., 1914, i, 981). The corresponding chloro-compound forms white needles, m. p. 119°, and the iodo-derivative separates in very pale yellow prisms, m. p. 102°. If the bromo-ketone is heated with sodium acetate and acetic anhydride, it yields the diacetate (glistening scales, m. p. 86°) of 2-hydroxy-4-methoxyphenyl hydroxymethyl ketone, this being obtained in colourless plates, m. p. 128°, by hydrolysis with alcoholic potassium hydroxide. The latter is the methyl ether of fisetol, but no method has been devised whereby the methoxyl group can be exchanged for hydroxyl.

J. C. W.

**Pungent Principles of Ginger. I. Zingiberone.** (A Correction.) HIROSHI NOMURA (*Sci. Rep. Tohoku Imp. Univ.*, 1918, 6, 375).—The ketone, isolated from ginger, to which, in a previous paper (*ibid.*, 1917, 6, 41), the name zingiberone was assigned, bears no relation to the zingiberol obtained by Brooks (A., 1916, i, 408), and in order to avoid confusion the name zingerone is substituted for zingiberone (compare T., 1917, 111, 769; Lapworth, Pearson, and Royle, *ibid.*, 777). H. M. D.

**Oxidation of Diaminophenols.** JEAN PICCARD and LOUIS M. LARSEN (*J. Amer. Chem. Soc.*, 1918, 40, 1079–1092).—Holoquinonoid aminobenzoquinoneimine salts have been prepared with the purpose of comparing their colours with those of other holoquinonoid and of meriquinonoid salts. It is found that the auxochromic effect of an anilino-group is, unlike the cases of other holoquinonoid salts, the same as that of a dimethylamino-group. 2-Amino-p-benzoquinone-4-imine hydrochloride,



which separates when an aqueous solution of 2:4-diaminophenol dihydrochloride is oxidised by 4*N*-ferric chloride at 0°, and the solution is further cooled to -15°, crystallises in two forms, unstable, pale red needles and stable, dark red plates with a green surface colour; it is rapidly decomposed by water, is proved to be holoquinonoid by titration with titanium trichloride, forms red solutions in water or alcohol, which are changed to yellow by concentrated sulphuric acid owing to salt-formation at the amino-group, and gives a spectrum showing general absorption in the violet region. The quinonoid perchlorate was obtained in pale red needles (not quite pure) which exploded violently when heated. The quinonoid nitrate was obtained by oxidising with 2*N*-ferric nitrate instead of with 4*N*-ferric chloride; it is more stable than the hydrochloride and exists in only one modification, bright red needles. 2-Dimethylamino-p-benzoquinone-4-imine perchlorate,  $\text{O}:\text{C}_6\text{H}_3(\text{NMe}_2):\text{NH}, \text{HClO}_4$ , is obtained by oxidising 4-amino-2-dimethylaminophenol dihydrochloride with 4*N*-ferric chloride at 0°, adding a saturated solution of sodium perchlorate, and cooling to -20°; it crystallises in pale red needles which slowly darken on keeping, forms violet-red solutions, is unchanged by strong acids except concentrated sulphuric acid, in which it dissolves to a pale yellow solution, becoming violet-red again on dilution, and gives a flat absorption curve with a wide maximum in the green. The picrate crystallises in long, dark brown needles, and forms red solutions in alcohol and acetone.

3-Amino-6-hydroxydiphenylamine, colourless crystals which rapidly oxidise in air, obtained by the electrolytic reduction of *m*-nitrodiphenylamine in concentrated sulphuric acid (1.5 amps, 6.5 volts, electrode 15 sq. cm.), is isolated as the dihydrochloride, unstable, hygroscopic crystals, which in 50% acetic acid at 0° is oxidised by 4*N*-ferric chloride, the addition of picric acid in glacial acetic acid to the resulting violet solution yielding 2-anilino-p

*orthoquinone-4-imine picrate*,  $\text{O}:\text{C}_6\text{H}_3(\text{NHPh})\cdot\text{NH}\cdot\text{C}_6\text{H}_4(\text{NO}_2)_2\cdot\text{OH}$ . Its salt forms a microcrystalline powder, yields red solutions in alcohol and acetone, and dissolves in dilute acids, forming violet solutions. Salts with the usual inorganic acids have not been obtained, on account of their instability in solution.

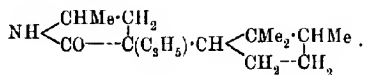
An orthoquinonoid structure of the preceding quinoneimine salts not impossible. C. S.

**Syntheses by Means of Sodamide. Preparation and study of some Monoalkyl and Dialkylcamphors and their derivatives.** A. HALLER and JEAN LOUVRIER (*Ann. Chim.*, 1918, x], 9, 189—251).—For the most part a more detailed account of work already published (compare A., 1914, i, 555). The following new compounds are described.

*Diethylcampholamide*, m. p. 75°, b. p. 185°/12 mm.,  $[\alpha]_D^{25} + 76^\circ 15'$  to  $77^\circ 5'$ , prepared by the action of sodamide on diethylcamphor in xylene, when acted on by nitrous acid yields *diethylcampholic acid*, m. p. 78°, b. p. 157°/20 mm.,  $[\alpha]_D^{25} + 60^\circ 59'$  to  $62^\circ 49'$ , giving a potassium salt. *Methylethylcampholamide*, m. p. 60°, b. p. 180°/14 mm.,  $[\alpha]_D^{25} + 75^\circ 42'$  to  $3^\circ 55'$ , yields *methylethylcampholic acid*, m. p. 74°,  $[\alpha]_D^{25} + 57^\circ 10'$  to  $55^\circ 24'$ .

*Allylborneol*, b. p. 119°/14 mm.,  $[\alpha]_D^{25} + 19^\circ 23'$  to  $20^\circ 22'$ , gives a *phenylurethane*, m. p. 64°.

*Diallylcamphor*, b. p. 155°/16 mm.,  $D_4^{20} 0.982$ ,  $[\alpha]_D^{17} + 148^\circ$  to  $52^\circ 22'$ ; *diallylborneol*, m. p. 47°,  $[\alpha]_D^{25} + 78^\circ 28'$ ; *diallylcampholamide* or 4(2': 2': 3')-trimethylcyclopentyl-2-methyl-4-allylpyrrolidone,  $\text{NH}_2\cdot\text{CO}\cdot\text{C}_8\text{H}_{11}\cdot\text{CH}(\text{C}_3\text{H}_5)_2$  or



b. p. 212°/15 mm.,  $[\alpha]_D^{25} 40^\circ 18'$ .

*Dibenzylcampholamide*, m. p. 121°,  $[\alpha]_D^{25} + 33^\circ 7'$  to  $34^\circ 18'$ .

*Benzylethylcampholamide*, m. p. 181°, b. p. 230—240°/12 mm.

*Ethylcampholenitrile*, b. p. 110°/11 mm.,  $D_4^{20} 0.903$ ,  $[\alpha]_D^{25} + 70^\circ 26'$ , gives in turn *ethylcampholenamide*, m. p. 62°, and *ethylcampholenic acid*, m. p. 36°, b. p. 157°/20 mm.

*Allylcamphoroxime*, m. p. 101°, b. p. 158°/16 mm.,  $[\alpha]_D^{25} + 58^\circ 10'$  to  $54^\circ 14'$ , gives a *phenylurethane*, m. p. 160°, and yields in turn *allylcampholenitrile*, b. p. 130°/11 mm.,  $D_4^{20} 0.934$ ,  $[\alpha]_D^{25} + 28^\circ 47'$ ; *allylcampholenamide*, m. p. 97°; and *allylcampholenic acid*, m. p. 19°, b. p. 156°/16 mm.

*Propylcamphoroxime* yields *propylcampholenitrile*, b. p. 124°/11 mm.,  $D_4^{20} 0.907$ ,  $[\alpha]_D^{25} + 46^\circ 18'$ ; *propylcampholenamide*, b. p. 173°/12 mm.; and *propylcampholenic acid*, b. p. 160°/12 mm.

*Benzylcamphoroxime* gives *benzylcampholenitrile*, b. p. 195°/14 mm.,  $[\alpha]_D^{25} + 54^\circ 14'$  to  $+43^\circ 58'$ , according to the method of preparation; *benzylcampholenamide*, b. p. 197°/12 mm., and *benzylcampholenic acid*, m. p. 68°, b. p. 204°/12 mm., which gives a sodium salt. W. G.



**The Wagner Rearrangement.** L. RUZICKA (*Helvetica Chim. Acta*, 1918, 1, 110—133).—It is shown that whilst methyl- $\alpha$ -fenchocamphorol and methylcamphenilol apparently do not undergo the Wagner rearrangement when heated with sodium hydrogen sulphate, methylborneol and methylfenchyl alcohol, despite their marked difference in structure, give the same reaction products after the removal of water, namely, fenchone and camphor. These results go to show that of the two possible explanations of the Wagner rearrangement, that demanding the intermediate formation of a tricyclic ring is the more correct. The apparent contradiction underlying this explanation can be elucidated in the following way, and a further proof of the tricyclic theory advanced at the same time. Whereas the tricyclics derived from borneol and fenchyl alcohol are different substances, it is found that the tricyclics obtained from their homologues, methylborneol and methylfenchyl alcohol, must be identical. It is therefore clear that in this case the further products of the reaction must also be identical. The formation of this common tricyclic from compounds of the fenchone and camphor types is to be attributed to the fact that the single linkings of the tricyclic three-membered ring exhibit different stabilities towards sodium hydrogen sulphate. Generally, the linking which leads to the fenchone type is opened, whilst that leading to the camphor type is more stable; the third linking, which would lead to an unknown type, is not opened. A consideration of the tricyclics obtainable from the other alcohols shows that otherwise quite different isomeric alcohols yield the same tricyclic. This will explain why methylcamphenilol apparently does not undergo rearrangement on removing water. The tricyclic obtained is identical with that furnished by borneol, and consequently the only product of the reaction is camphene. With regard to the further rupture of the three-membered ring of the tricyclic, the author gives the following generalisations:

(1) Of the linkings of the three-membered ring of the tricyclics, that is the weakest which lies between the two carbon atoms where the difference between the numbers of directly connected hydrogen atoms is greatest.

(2) Should two bonds be similar in the above respect, then that one will be opened which at the same time opens the five-membered ring with the largest number of quaternary carbon atoms.

A number of tables showing the relationships are included in the paper.

J. F. S.

**Constituents of Resins. I. Siarresinol from Siamese Gum Benzoin.** ALOIS ZINKE and HANS LIEB (*Monatsh.*, 1918, 39, 95—105).—Siarresinol from Siamese gum benzoin (Reinitzer, A., 1915, i, 431) is probably identical with the benzoresinol obtained by Lüdy from the same source (A., 1893, i, 666); it gives an additive compound with acetic acid,  $C_{30}H_{48}O_4 \cdot C_2H_4O_2$ , needles, m. p. 280—281.5°, and a benzoyl derivative, needles, m. p.

182—183°,  $[\alpha]_D^{20} + 30.0^\circ$  (ethyl alcohol), which on hydrolysis regenerates siareesinol. D. F. T.

**The Isolation of Pigments by Means of Picric and Dichloropicric Acids.** RICHARD WILLSTÄTTER and GUSTAV SCHUDEL (*Ber.*, 1918, 51, 782—788).—In devising a method for the extraction of plant pigments, Willstätter has already had a certain measure of success with a process which depends on the partition of the dye between water and amyl alcohol (compare A., 1917, i, 42—50). The serious limitation to this method is that only non-glucosidic pigments are efficiently extracted, diglucosides often being left entirely in the aqueous layer. If picric acid is added to the solution, a wider range of pigments can be transferred, as picrates, to other, non-miscible solvents. Thus, ether will only dissolve the picrates of non-glucosidic pigments; diethyl ketone will not remove the diglucoside picrates, but extracts monoglucoside picrates to the extent of about 50% of the quantity present; whilst a mixture of amyl alcohol (2 parts) and acetophenone (1 part) will remove all the monoglucosides and 70—80% of the diglucosides as picrates.

The use of picric acid has this drawback, however, that the picrates are usually not very soluble in organic media. Dichloropicric acid is much superior in this respect, although it is so much more soluble in water that the expenditure of reagent is greater. By the use of this acid, rosaniline and pararosaniline can be completely extracted from aqueous solutions by ether; safranin by diethyl ketone; methylene-blue by ether, the picrate crystallising soon in bronzy prisms; and mono- and di-glucosidic pigments can be removed completely by one extraction with a mixture of amyl alcohol and acetophenone (2:1).

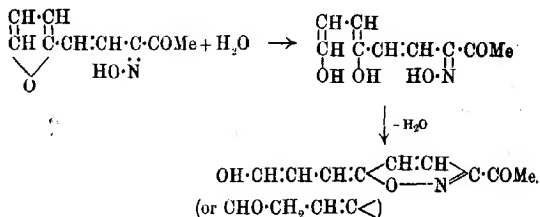
No actual example of the use of dichloropicric acid is given, but the occasion serves to describe its preparation. *p*-Nitroaniline is chlorinated by Flürscheim's method (T., 1908, 93, 1772), the 2:6-dichloro-4-nitroaniline is converted into 3:5-dichloro-1-nitrobenzene (Holleman, A., 1905, i, 41), and this is reduced to the amine by means of iron filings and hydrochloric acid, and then transformed into 3:5-dichlorophenol, which is nitrated by means of fuming nitric acid and acetic acid. Dichloropicric acid (3:5-dichloro-2:4:6-trinitrophenol) crystallises in pale yellow prisms, m. p. 139—140° (corr.) (compare Blanksma, *Rec. trav. chim.*, 1908, 27, 25, 36), the sodium salt in quadratic prisms, and the potassium salt in slender needles, both being lemon-yellow. The solubilities in water at 19.7° are 7.4, 7.4, and 0.55 grams per 100 c.c., for the acid, Na and K salt, respectively.

The conversion of 3:5-dichloroaniline into 3:5-dichlorophenol is carried out by adding the solution of the diazonium sulphate to a boiling mixture of concentrated sulphuric acid, water, and anhydrous sodium sulphate (proportions, 9:5:6). If Blanksma's method is adopted (*ibid.*), the following by-products arise: 3:5-

*dichloro-4-3':5'-dichlorobenzeneazophenol*, brownish-red, flat, silky prisms, m. p. 191—192° (corr.), and 3:5-*dichloro-2:4-bis-3':5'-dichlorobenzeneazophenol*,  $\text{OH}\cdot\text{C}_6\text{H}_3(\text{N}:\text{N}\cdot\text{C}_6\text{H}_3\text{Cl}_2)_2$ , long, glistening, orange needles, m. p. 260—261° (corr.), both of which form sodium salts which dissolve in ether; and 3:5-*dichloro-4-nitroso-phenol*, very pale greenish-yellow prisms, m. p. 150—151° (corr.).  
J. C. W.

**Isomerism of Furfurylidenediacetyl Monoxime** [ $\beta$ -2-Furyl-vinyl Acetyl Ketoxime]. OTTO DIELS and HERMANN ROEHLING (*Ber.*, 1918, 51, 828—836. Compare A., 1913, i, 875).—The product of the condensation of furfuraldehyde with dimethyl diketone monoxime, namely,  $\beta$ -2-furylvinyl acetyl ketoxime, yields an *acetate*,  $\text{C}_8\text{H}_9\text{O}\cdot\text{CH}:\text{CH}\cdot\text{C}\cdot\text{Ac}\cdot\text{N}\cdot\text{OAc}$ , prisms, m. p. 141°, which is transformed by warming with 33% potassium hydroxide into the salt of  $\beta$ -2-furylacrylic acid,  $\text{C}_8\text{H}_9\text{O}\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$ .

When added to concentrated hydrochloric acid, the oxime rapidly dissolves with a deep olive-green colour, changing to brown, and then deposits crystalline leaflets of the *hydrochloride*, decomp. 128—129°, of an isomeric *base*, which is supposed to be formed by the hydrolytic rupture of the furan ring, followed by ring closure in a new position, thus:



The base crystallises in greenish-yellow needles, m. p. 145°, dissolves in concentrated hydrochloric acid and in dilute alkali hydroxides or carbonates, reduces Fehling's and ammoniacal silver solutions immediately, gives a deep violet-red coloration with alcoholic ferric chloride, which soon disappears, owing to reduction, but remains permanganate-coloured on adding an excess of the reagent, forms a deep red compound with benzenediazomium chloride, and yields the following characteristic derivatives: (a) with methyl chloroformate, a *carbomethoxy*-compound, white needles, m. p. 128—129°; (b) a *p-nitrophenylhydrazone*, brownish-red, slender, curved needles, decomp. 136—137°; (c) with methylamine, a *product*,  $\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}_2$ , pale yellow needles, m. p. 175° (decomp.), and a substance crystallising in stout, chromate-red rhombohedra, m. p. 183°. When boiled with an excess of water or dilute sulphuric acid, or heated with methyl iodide at 100°, the base changes into a third isomeride, namely, 3-*acetyl-5-2'-furyl-4:5-*

*dihydroisooxazole*,  $C_4H_3O \cdot CH \begin{smallmatrix} CH_2 \cdot CAc \\ \diagup \quad \diagdown \\ O \quad N \end{smallmatrix}$ , which crystallises in soft, white needles, m. p. 103—104°. J. C. W.

**$\beta$ -Phenylcoumarins.** ADOLF SONN (*Ber.*, 1918, 51, 821—827).—Some years ago, von Meyer stated that 3-hydroxyflavone is produced when benzoacetodinitrile,  $NH \cdot CPh \cdot CH_2 \cdot CN$ , is condensed with resorcinol under the influence of hydrogen chloride (A., 1903, i, 482). It is known that dinitriles of this type readily change into acylacetoneitriles on treatment with acids, and therefore it might be expected that the above result would be achieved if  $\omega$ -cyanoacetophenone,  $COPh \cdot CH_2 \cdot CN$ , were substituted for the dinitrile. Bargellini and Forli-Forti have already studied the condensation of compounds of this type with phenols, and proved that the products are  $\beta$ -phenylcoumarins and not flavones. This led the author to suspect that von Meyer had wrongly interpreted his result, and he has found, on repeating the experiment, that the product is not 3-hydroxyflavone, but 7-hydroxy-4-phenylcoumarin (Pechmann and Hancke, A., 1901, i, 210).

In their condensations, Bargellini and Forli-Forti used zinc chloride, and were not very successful. It is better to dissolve the materials in glacial acetic acid and to employ hydrogen chloride as the condensing agent. Thus, *p*-cyanoacetylanisole and phloroglucinol yield 5 : 7-dihydroxy-4-*p*-methoxyphenylcoumarin, which crystallises in flat prisms, m. p. 262°, and forms a *diacetate*, glistening, elongated tablets or flat prisms, m. p. 189—190° (the Italian authors gave m. p. 179—180°). If ether is used as solvent, a different product is formed, most probably the corresponding *imino-ether*,  $C_6H_2(OH)_2 \begin{smallmatrix} O \\ \diagup \quad \diagdown \\ C(C_6H_4 \cdot OMe) : CH \end{smallmatrix} \cdot C : NH$ , stout, pale yellow crystals, decomp. above 300°, since it yields the coumarin on warming with water or dilute acids.

The dinitrile corresponding with *p*-cyanoacetylanisole, namely, *p*-methoxybenzimidocetonitrile,  $OMe \cdot C_6H_4 \cdot C(NH) \cdot CH_2 \cdot CN$ , is obtained in colourless, stout prisms, m. p. 119°, by the interaction of anisonitrile and acetonitrile in the presence of sodium. The primary sodium salt being decomposed by water. J. C. W.

**Synthesis of Ketones in the Thiophen Series.** V. THOMAS and V. COUDERC (*Bull. Soc. chim.*, 1918, [iv], 23, 288—291).—Magnesium thienyl iodide reacts with nitriles, giving products which when treated with water give good yields of ketones. The following have been prepared by this method: ethyl thienyl ketone: phenyl thienyl ketone, dithienyl ketone;  $\alpha$ -naphthyl thienyl ketone, b. p. 187—188°/25 mm.; and  $\beta$ -naphthyl thienyl ketone, colourless needles, m. p. 87°. W. G.

**Synthesis of 1-Methyltetrahydropyridinecarboxylic Acids. I. A New Method for Preparing Arecaidine and Arecoline. Elucidation of the Constitution of Guvacine and Arecaine.** KURT HESS and FRIEDRICH LEIBBRANDT (*Ber.*, 1918, 51, 806—820).—When the 1-methylpiperidinecarboxylic acids are brominated in

methyl or ethyl alcohol and the products are heated with sodium alkyl oxides, 1-methyltetrahydropyridinecarboxylic acids are produced. These are closely related to the alkaloids of the areca (betel) nut.

Nipecotinic acid (piperidine-3-carboxylic acid) forms a fairly stable *acetate*, needles, m. p. 289–290° (decomp.). The following new derivatives of 1-methylpiperidine-3-carboxylic acid (compare A., 1917, i, 354) have been prepared: from the methyl ester (dihydroarecoline), the *hydrochloride*, needles, m. p. 193° (decomp.); methiodide, prismatic plates, m. p. 192°; and methoaurichloride, m. p. 123° (compare Willstätter, A., 1897, i, 385); also the *ethyl ester*, b. p. 101–102°/24 mm., and green *copper salt*.

Methyl 1-methylpiperidine-3-carboxylate is converted as indicated above into methyl 1-methyl-1:2:5:6-tetrahydropyridine-3-carboxylate, which is identical with arecoline, as the corresponding free acid is identical with arecaidine. The latter forms a *hydrobromide*, needles, m. p. 197° (decomp.).

Two other areca-nut alkaloids have been registered, namely, guvacine and its *N*-methyl derivative, arecaine (Jahns, A., 1891, 94, 1520). Assuming that these must be closely related to arecaidine, the authors have prepared 1-methyl-1:4:5:6-tetrahydropyridine-2-carboxylic acid from 1-methylpiperidine-2-carboxylic acid in the same way. This very closely resembles, but is not identical with, arecaine. *Methyl 1-methylpiperidine-2-carboxylate*, from pipecolinic acid acetate (*loc. cit.*), has b. p. 92–95°/21 mm., and the *hydrochloride* of the ethyl ester (*ibid.*) has m. p. 204° (decomp.). *1-Methyl-1:4:5:6-tetrahydropyridine-2-carboxylic acid* crystallises from pure alcohol in well-developed, quadratic, prismatic tablets, m. p. 213–214° (arecaine is insoluble in alcohol and has m. p. 231°), and forms a *hydrochloride*, m. p. 210°, readily soluble in alcohol (arecaine hydrochloride has m. p. 250° and is sparingly soluble), a *platinichloride*, orange-yellow prisms, m. p. 220° (arecaine platinichloride forms octahedra), an *aurichloride*, m. p. 200°, a *methyl ester*, and an *ethyl ester*, b. p. 96°/17 mm., both of which are limpid, highly refractive, pleasant-smelling oils.

The relationship between guvacine and arecaine is definitely established by methylating the former by the author's method, using formaldehyde and formic acid. The pure arecaine and its salts thus obtained had somewhat different properties from those quoted by Jahns; the new data are given above in brackets. When arecaine is boiled with alcoholic hydrogen chloride, it loses its methyl group and forms the *ethyl ester* of guvacine, b. p. 116°/19 mm., instead of its own ethyl ester. This oil reduces alkaline permanganate and absorbs bromine immediately.

This esterification of arecaine proves one thing, however, namely, that a carboxyl group is present in these alkaloids. That they also contain an ethylene linking is proved by the reduction of guvacine with hydrogen and colloidal platinum, when "dihydroguvacine" is formed. This is identical with *isonipecotinic acid* (piperidine-4-carboxylic acid). Consequently, guvacine is a tetrahydro-

pyridine-4-carboxylic acid, probably the 1:2:5:6-isomeride, and arecaine is its 1-methyl derivative.

J. C. W.

**Guvacine Methyl Ester (Guvacoline) and its Occurrence in Nature.** KURT HESS (*Ber.*, 1918, 51, 1004—1006).—The alkaloids of the areca nut include arecaine and its methyl ester, arecoline, guvacine and its *N*-methyl derivative, arecaine, and also the methyl ester of guvacine, which is designated "*guvacoline*." A specimen of the *hydrobromide* of this, crystallising in short prisms, m. p. 144—145°, has been provided by Messrs. Merck, and proved to have the above constitution by hydrolysis to guvacine and by esterification of this alkaloid.

J. C. W.

**Guvacine.** KARL FREUDENBERG (*Ber.*, 1918, 51, 976—982).—Independent of Hess, and without reference to his work (preceding abstracts), the author has investigated guvacine, and draws the conclusion that it is demethylated arecaine, or 1:2:5:6-tetrahydropyridine-3-carboxylic acid. If this is so, then arecaine and arecaine are identical.

The above acid was synthesised by Wohl and Losanitsch (*A.*, 1908, i, 47), and there is good agreement between the decomposition temperatures of the hydrochlorides, aurichlorides, and platinichlorides of this and guvacine. Guvacine *methyl ester*, b. p. 114° (corr.)/13 mm., forms a *hydrochloride*, hygroscopic leaflets, m. p. 121—122° (corr.), a *platinichloride*, silky, golden leaflets, m. p. 211° (corr.), and a *methiodide*. The latter has the same m. p. as arecoline *methiodide*, and yields arecaine on hydrolysis, there being again good agreement in the decomposition temperatures of the salts of the natural alkaloid and the present material.

1-*p*-Toluenesulphonylguvacine crystallises in stout plates, m. p. 167—168° (corr.), and is oxidised by alkaline permanganate to a (3 : 4)-*dihydroxy*-1-*p*-toluenesulphonylpiperidine-(3)-carboxylic acid, leaflets, m. p. 213—214° (corr.; decomp.), and by ozone in 95% acetic acid to a dicarboxylic acid, probably of the formula  $C_7H_7 \cdot SO_2 \cdot N < \begin{matrix} CH_2 \cdot CH_2 \cdot CO_2H \\ CH_2 \cdot CO_2H \end{matrix}$ , which crystallises in prisms and plates, m. p. 164° (corr.).

J. C. W.

**A New Volatile Alkaloid of the Common Broom.** AMAND VALEUR (*Compt. rend.*, 1918, 167, 163—164. Compare this vol., i, 350).—After separation of the alkaloids sparteine and sarracine (*loc. cit.*) from the mother liquors in the manufacture of sparteine sulphate, a new alkaloid was obtained by the addition of excess of alkali and extraction with ether. The new alkaloid, *senisteine*,  $C_{16}H_{28}N_2$ , has m. p. 60·5°, b. p. 139·5—140·5°/5 mm. (corr.), 177—178°/22 mm. (corr.), and yields a *hydrate*,

$C_{16}H_{28}N_2 \cdot H_2O$ ,  
 $\alpha_D^{20} - 52\cdot3^\circ$  (in alcohol), a *picrate*,  $C_{16}H_{28}N_2 \cdot 2C_6H_5(NO_2)_3 \cdot OH$ ,  
 a. p. 215° (decomp.), a *platinichloride*,  
 $C_{16}H_{28}N_2 \cdot 2HCl \cdot PtCl_4 \cdot 2\frac{1}{2}H_2O$ ,

u\*

decomposing at  $235^{\circ}$ , and an aurichloride,  
 $2(\text{C}_{16}\text{H}_{23}\text{N}_3, 2\text{HCl}), 3\text{AuCl}_3$ ,  
 yellow prisms, m. p.  $188^{\circ}$  (decomp.). This alkaloid is saturated  
 and does not contain a methyl group attached to nitrogen.

W. G.

**The Alkaloids of the Pomegranate Tree. V. Resolution of Pelletierine and Methylisopelletierine into their Optical Antipodes. Elucidation of Tanret's Bases.** KURT HESS and ANNALIESE EICHEL (*Ber.*, 1918, 51, 741—747. Compare this vol., i, 34).—Pelletierine and methylisopelletierine have been resolved by means of their tartrates. The bases were first treated with the *d*-acid, the solutions evaporated in a vacuum desiccator to syrupy consistency, and then mixed with alcohol, when the salt of the *d*-base separated, and then the *l*-base was recovered from the mother liquor and converted into the *l*-tartrate.

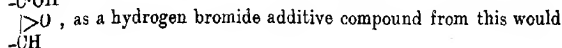
*d*-Pelletierine *d*-tartrate has m. p.  $129^{\circ}$ ,  $[\alpha]^{20} + 19.48^{\circ}$ , and *l*-pelletierine *l*-tartrate has m. p.  $129^{\circ}$ ,  $[\alpha]^{20} - 19.62^{\circ}$ . The active bases suffer considerable racemisation on distillation, but they may be isolated and converted into solutions of their sulphates with constant rotation,  $[\alpha]^{18} + 5.39^{\circ}$  and  $-5.33^{\circ}$  respectively. *d*-Methylisopelletierine *d*-tartrate has m. p.  $133-134^{\circ}$ ,  $[\alpha]^{20} + 19.12^{\circ}$ , and *l*-methylisopelletierine *l*-tartrate has m. p.  $132-134^{\circ}$ ,  $[\alpha]^{18} - 19.37^{\circ}$ . The free bases, in this case, are not subject to racemisation when distilled, resembling in this respect the parent alkaloid, coniine. The difference is probably due to the position of the oxygen atom, the side-chain being  $-\text{CH}_2\text{CH}_2\text{CHO}$  in the case of pelletierine and  $-\text{CO}\text{CH}_2\text{CH}_3$  in the other case. *d*-Methylisopelletierine has b. p.  $109^{\circ}/24$  mm.,  $[\alpha]^{18} + 6.71^{\circ}$  (solution in *N*-sulphuric acid),  $+ 9.90^{\circ}$  (solution in hydrochloric acid), and the *l*-base has practically the corresponding constants. (The light employed was that of an incandescent gas lamp.)

Among the alkaloids of the pomegranate, Tanret described some optically active forms of the above bases, but the rotations reported by him were much greater than those observed with the resolved alkaloids. The authors feel quite convinced that no active modifications are present in the root, for they have not found optical activity to be displayed by any of their fractions, either before or after distillation.

J. C. W.

**Degradation of Scopoline. III. Scopoline  $\rightarrow$  Hydroscopoline  $\rightarrow$  Tropan.** KURT HESS (*Ber.*, 1918, 51, 1007—1015. Compare A., 1916, i, 285, and Schmidt, *ibid.*).—It has been suggested already that hydroscopolina is a dihydroxytropan. Hydroxytropans are found to resist reduction by ordinary methods, but when heated with concentrated hydriodic acid and a considerable excess of phosphonium iodide at  $200^{\circ}$ , they suffer replacement of hydroxyl by hydrogen fairly readily. Thus tropine yields tropan and nortropine gives nortropan, whilst hydroscopoline also forms tropan, which supports the above assumption.

Of the two oxygen atoms in scopoline, one is known to be present in a hydroxyl group and the other is probably included in an oxide ring. The comparative ease with which scopoline combines with hydrogen bromide and parts with it again on treatment with alkalis suggests the oxidic structure, but there can scarcely be an ethylene-oxide arrangement such as Schmidt proposed, thus,



as a hydrogen bromide additive compound from this would be very unstable, which hydroscopoline bromide is not. The author believes that the oxygen atom in question bridges across from the pyrrolidine ring to some carbon atom in the piperidine ring.

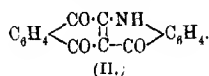
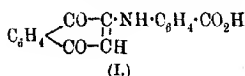
When hydroscopoline bromide hydrobromide is boiled with concentrated hydrochloric acid, it yields *hydroscopoline chloride hydrochloride*,  $\text{C}_8\text{H}_{14}\text{O}_2\text{NCl}\cdot\text{HCl}$ , needles, m. p.  $289^\circ$ . (decomp.). Many attempts have been made to oxidise this salt, in the hope of obtaining a chloroscopolic acid, but, almost always, the only product was found to be scopoline. With silver oxide and hot water, however, the strange result was the elimination of the *N*-methyl group, scopoline being obtained.

A convenient method for the preparation of hydroscopoline is described. J. C. W.

**The Linear Phenonaphthacridonequinone and Quinacridonequinone.** W. ST. LESNIAŃSKI (*Ber.*, 1918, **51**, 695—706).

These compounds have been synthesised in order to determine whether quinones of the acridone series resemble anthraquinone derivatives in being vat dyes, which is found to be the case.

Anthranilic acid and  $\alpha$ -naphthaquinone are heated together in alcoholic solution, when *o*-2-naphthaquinonylamino benzoic acid (I) is formed. This crystallises in red needles, m. p.  $271^\circ$  (corr.), forms a dark red silver salt, and yields *phenonaphthacridonequinone* (II) on heating with concentrated sulphuric acid at  $140$ — $150^\circ$ .

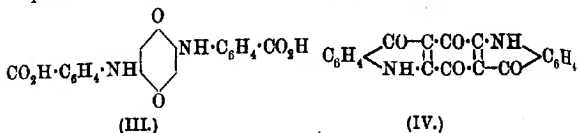


The quinone sublimes in orange needles, m. p.  $384^\circ$ , forms a red potassium salt,  $\text{C}_{17}\text{H}_8\text{O}_3\text{NK}\cdot\text{H}_2\text{O}$ , and gives compounds with various acids, of which the *nitrate*,  $\text{B}_2\text{HINO}_3$ , pale yellow needles, is an example. On distillation with zinc dust, it yields dihydrophenonaphthacridine, m. p.  $285$ — $286^\circ$  (Schöpf, A., 1895, i, 107), whilst reduction with sodium hyposulphite gives *dihydrophenonaphthacridonequinone* as a reddish-violet powder, m. p.  $317^\circ$  (corr.), which forms blue solutions in alkali hydroxides, from which cotton is dyed orange-yellow, and yields an orange *acetyl* derivative, m. p.  $392^\circ$  (corr.). *Dinitrophenonaphthacridonequinone*, a yellow powder, m. p.  $299^\circ$  (corr.), is obtained by the action of a warm mixture of fuming nitric and sulphuric acids.

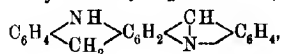
The other quinone is obtained by heating benzoquinoned-



anthranilic acid (III) (Ville and Astre, A., 1895, i, 465) with sulphuric acid at 145—155°. *Quinacridonequinone* (IV) is an

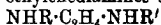


amorphous, yellow powder, which partly sublimes and decomposes, without melting, at above 530°, and is insoluble even in solvents of high b. p. It forms a red, crystalline, *potassium* salt,  $\text{C}_{20}\text{H}_8\text{O}_4\text{N}_2\text{K}_2\text{H}_2\text{O}$ , and an amorphous, brownish-yellow, *dipotassium* salt,  $\text{C}_{20}\text{H}_8\text{O}_4\text{N}_2\text{K}_2\text{H}_2\text{O}$ , both of which are very easily hydrolysed, and it also yields an unstable *nitrate*,  $\text{B}_3\text{HNO}_3$ , long, golden-yellow needles, and a crystalline *sulphate*,  $\text{B}_3\text{H}_2\text{SO}_4$ . The quinone is practically indifferent to the action of alkalis, acylating, or ketone reagents, but yields *dihydroquinacridine*,



as a dark red, lustrous powder, m. p. 379° (corr.; decomp.), when distilled with zinc dust. It may also be reduced by means of sodium hyposulphite, but the bluish-violet product is insoluble. On warming with fuming nitric acid, it yields *dinitroquinacridonequinone*,  $\text{C}_{20}\text{H}_8\text{O}_4\text{N}_2(\text{NO}_2)_2$ , as a pale yellow, insoluble powder, which forms a dark red *potassium* salt,  $2\text{H}_2\text{O}$ . J. C. W.

**Bromoalkylated Aromatic Amines. III. Derivatives of Ethylenediamine.** J. VON BRAUN, K. HEIDER, and E. MÜLLER (*Ber.*, 1918, 51, 737—741. Compare this vol., i, 107, 269).—The  $\omega$ -bromoethyl derivatives of secondary amines react with other secondary bases to form compounds of the general formula  $\text{C}_6\text{H}_5\cdot\text{NR}\cdot\text{C}_2\text{H}_4\cdot\text{NR}'\text{R}''$ , where  $\text{R}'$  and  $\text{R}''$  may be both aliphatic radicles or one of them aromatic. The nitroso-derivatives of these may be deprived of the aromatic residues by hydrolysis, thus giving rise to alkylated ethylenediamines of the types



or  $\text{NHR}\cdot\text{C}_2\text{H}_4\cdot\text{NR}'\text{R}''$ , some of which are now described. The syntheses are comparatively simple and doubtless of manifold applicability.

*s*-Diphenyldimethylethylenediamine (*loc. cit.*, 108) gives a pale green *dinitroso*-compound,  $\text{C}_6\text{H}_4(\text{NMe}\cdot\text{C}_6\text{H}_4\cdot\text{NO})_2$ , m. p. 208°, which forms an almost insoluble, greenish-brown *monohydrochloride*, m. p. 153°, and is hydrolysed by boiling with sodium hydrogen sulphite solution (D 1'21) to *s*-dimethylethylenediamine, m. p. 119° (Schneider, A., 1896, i, 200).

Methyl- $\beta$ -bromoethylaniline (this vol., i, 108) reacts with ethylaniline or ethyl- $\beta$ -bromoethylaniline (this vol., i, 270) with methylaniline to form *NN'-diphenyl-N-methyl-N'-ethylethylenediamine*,  $\text{NMePh}\cdot\text{C}_2\text{H}_4\cdot\text{NEtPh}$ , as a viscous liquid, b. p. 232—234°/21 mm.,

which gives a *picrate*, m. p. 176°, a *pp'-dibromo-compound*, needles, m. p. 100°, and a yellowish-green *dinitroso-derivative*, m. p. 190°. The latter is hydrolysed as above to *s-methylethylenediamine*, a mobile oil, b. p. 133°, which fumes in the air and forms a very hygroscopic *hydrochloride*,

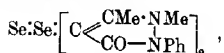
$\text{NHMe}\cdot\text{C}_2\text{H}_4\cdot\text{NHMe}\cdot 2\text{HCl}$ ,  
m. p. 217–218°, and a *platinichloride*, m. p. 240°.

Phenyltrimethylethylenediamine (this vol., i, 108) likewise gives rise to *trimethylethylenediamine*,  $\text{NHMe}\cdot\text{C}_2\text{H}_4\cdot\text{NMe}_2$ , which has b. p. 140° (about) and forms a very hygroscopic *hydrochloride*, m. p. 183°, a *platinichloride*, yellowish-red spikes from water, in which it is freely soluble, m. p. 230° (decomp.), and a *picrate*, m. p. 209–210°.

J. C. W.

**New Selenium Derivatives of Antipyrine.** FRITZ VON KONEK and OSKAR SCHLEIFER (*Ber.*, 1918, 51, 842–855).—The action of the selenium chlorides on antipyrine is described.

The monochloride reacts as though it were “*selenoselenyl dichloride*,”  $\text{Se}\cdot\text{SeCl}_2$ . When a solution in carbon tetrachloride is added to a concentrated solution of antipyrine in chloroform at 0°, *diantipryl diselenide* (or *selenoselenide*),



is deposited. This crystallises from about 40% alcohol in yellow needles, m. p. 215–216°, and deposits elementary selenium when boiled with hydrochloric acid, the solution containing the salt of *diantipryl selenide*. This compound is precipitated by the addition of sodium carbonate; it crystallises from benzene in pearly flakes, m. p. 240°, and forms a *dihydrochloride* and a compound with mercuric chloride. It may be identical with a substance mentioned in D.R.-P. 299510 (1917), obtained from antipyrine by the action of selenium dioxide and concentrated sulphuric acid.

Selenium tetrachloride also reacts vigorously, giving *diantipryl-selenium dichloride*,  $(\text{C}_{11}\text{H}_{11}\text{ON}_2)_2\text{SeCl}_2$ , which crystallises from benzene in pearly scales, m. p. 225°, and changes into the above selenide on treatment with alkalis.

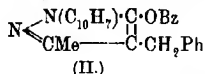
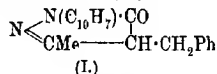
Some notes on the analysis of organo-selenium compounds are given in an appendix. For the estimation of carbon and hydrogen, the long combustion tube is filled with copper oxide and lead chromate in equal layers, with a layer of lead peroxide, about 12–15 cm. long, kept at 180–200°, in the front. The various methods for estimating selenium have been tested, but not one is found to be entirely satisfactory. Oxidation with nitric acid or nitric acid and potassium chlorate is accompanied by loss of selenium in the fumes; for the oxidation by sodium peroxide, a large excess of the reagent must be used, otherwise some free selenium will be obtained, and the quantitative reduction of the sodium selenate formed to the element cannot be achieved; combustion in oxygen in a bomb sometimes results in loss by the

alloying of selenium with the platinum wires and also the production of oxides other than the desired selenic oxide (see this vol., ii, 309). Frerich's method (decomposition with fuming nitric acid in the presence of silver nitrate, evaporation, filtration of the silver selenite, and titration of this in dilute nitric acid solution by means of a thiocyanate solution) gave correct results in the above cases, but it was also found to be convenient to digest the compound with pure sulphuric acid (10 c.c. for 0.2 gram) until a brownish-green colour developed, then to dilute to about 200 c.c., saturate with sulphur dioxide, leave overnight, and collect the precipitate of selenium. The drawback to this method is that it is difficult to tell just when to stop the action of the sulphuric acid, as it must not proceed to the production of much selenous acid.

J. C. W.

**Synthesis of some New Naphthylpyrazolones.** FRITZ VON KONEK and RICHARD MITTERHAUSER (*Ber.*, 1918, 51, 865—871).—The application of some naphthylhydrazines in the synthesis of pyrazolones is described.

$\beta$ -Naphthylhydrazine and ethyl benzylacetoacetate produces 1- $\beta$ -naphthyl-4-benzyl-3-methyl-5-pyrazolone (I), which crystallises in rosettes of pale pink needles, m. p. 153°, yields a *picrate*, canary-yellow, matted needles, and reacts with benzoyl chloride in the presence of sodium hydroxide solution to form the benzoate of its enolic modification, namely, 5-benzoyloxy-1- $\beta$ -naphthyl-4-benzyl-3-methylpyrazole (II), yellow needles, m. p. 138°. The same base

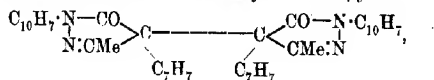


reacts with ethyl isopropylacetoacetate to form 1- $\beta$ -naphthyl-3-methyl-4-isopropyl-5-pyrazolone, small, pale yellow needles, m. p. 160° (*picrate*, yellow needles), and with crotonic acid to give

1- $\beta$ -naphthyl-3-methyl-5-pyrazolidone,  $\text{NH} \begin{array}{c} \diagup \text{N}(\text{C}_{10}\text{H}_7) \cdot \text{CO} \\ \diagdown \text{CHMe} \end{array} \text{---} \text{CH}_2$ , pale

brown crystals, m. p. 107°. Aceto- $\beta$ -naphthylhydrazide (from the base and acetamide) reacts with ethyl benzylacetoacetate and phosphorus trichloride to form 1- $\beta$ -naphthyl-4-benzyl-5-methyl-3-pyrazolone, yellow needles, m. p. 208°.

$\alpha$ -Naphthylhydrazine gives rise to 1- $\alpha$ -naphthyl-4-benzyl-3-methyl-5-pyrazolone, pale yellow rosettes, m. p. 168°, which forms a yellow *picrate* and reacts with nitrous acid to yield a *bis-pyrazolone*,



brown crystals, m. p. 215°.

*pp'*-Dihydrazinodiphenyl and ethyl benzylacetoacetate condense at 160° to form 4:4'-diphenylenebis-4-benzyl-3-methyl-5-pyrazolone,  $\text{C}_{34}\text{H}_{26}\text{O}_2\text{N}_4$ , as a yellow powder.

J. C. W.

**Synthesis of Iminouracil-6-acetic Acid.** DAVID E. WORRALL (*J. Amer. Chem. Soc.*, 1918, **40**, 1133—1135).—Guanidine carbonate and ethyl acetonedicarboxylate readily condense in boiling alcoholic solution to give a 90% yield of *guanidine 2-iminouracil-6-acetate*,  $\text{NH} \begin{array}{c} \diagup \text{CO} \text{---} \text{CH} \diagdown \\ \diagdown \text{C}(\text{NH}) \cdot \text{NH} \diagup \end{array} \text{C} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \cdot \text{CH}_5\text{N}_3$ , microscopic needles, decomp.  $213\text{--}214^\circ$  with formation of an amorphous solid, m. p.  $230^\circ$ . A solution of the salt forms with a solution of copper sulphate dark green, diamond-shaped crystals. *2-Iminouracil-6-acetic acid*, liberated from the guanidine salt by hydrochloric acid, crystallises from water in colourless, square plates, m. p.  $289\text{--}290^\circ$  (decomp.), decomposes soluble carbonates, reacts with bromine to form a substance, needles, m. p.  $210\text{--}211^\circ$  (decomp.), and with concentrated nitric acid at  $70^\circ$  to form an amorphous, yellow *5-nitro-derivative*, decomp.  $309\text{--}310^\circ$ . The sodium salt and copper sulphate solution yield a light green precipitate consisting of microscopic, pointed, twinned plates intersecting at right angles.

C. S.

**Hydrogen Peroxide as a Reagent in the Purine Group.**  
**II. Action of Hydrogen Peroxide on Uric Acid.** C. S. VENABLE (*J. Amer. Chem. Soc.*, 1918, **40**, 1099—1120. Compare Venable and Moore, this vol., i, 104).—The usual course of the experiments is to treat an aqueous solution of uric acid with a definite volume of *6N*-sodium hydroxide, to bring the mixture to the desired temperature, and to add the hydrogen peroxide, usually in 3% solution. At definite intervals, samples are taken and analysed. The temperature range is  $20\text{--}90^\circ$ , and the excess alkali concentration from 0 to *0.5N*. Three different products are formed, according to the experimental conditions. In weakly alkaline or neutral solutions and at temperatures near that of boiling water, allantoin is first formed in large quantities, together with smaller amounts of carbonyldicarbamide, but no genetic relationships connecting the two substances have been discovered; they appear to be products of two independent reactions. As the oxidation proceeds, the amount of carbonyldicarbamide remains fairly constant, but the yield of allantoin rapidly diminishes, with the appearance of increasing amounts of cyanuric acid up to a maximum yield of 10%. Increasing the alkalinity at this high temperature rapidly diminishes the yield of all three substances, until with an excess alkalinity of *0.1N* only very small amounts of cyanuric acid are obtained. At lower temperatures and in weakly alkaline solutions the same phenomena were observed, the disappearance of the allantoin being much slower. On increasing the alkalinity, the yield of cyanuric acid rapidly increased, with a corresponding decrease in the yields of both allantoin and carbonyldicarbamide. At  $20^\circ$  and with an excess alkalinity of *0.5N*, no allantoin or carbonyldicarbamide was observed, whilst the yield of cyanuric acid was as high as 50% of the theoretical. Further increase of alkalinity or lowering of the temperature was apparently without effect. The

preceding high yield of cyanuric acid required explanation, because it was found that under the experimental conditions allantoin was rapidly decomposed by hydrogen peroxide without producing cyanuric acid, and the largest yield of carbonyldicarbamide was 15%, which, assuming a quantitative conversion to cyanuric acid and adding the 10% of the latter already present, only accounts for a 30% yield of cyanuric acid. Furthermore, the conversion of 1 mol. of carbonyldicarbamide to 1 mol. of cyanuric acid requires the liberation of 1 mol. of ammonia, whereas the molecular ratio of ammonia formed to cyanuric acid recovered was found to be less than 1:3. Also, in all oxidations at low temperature and high excess of alkali, no allantoin or carbonyldicarbamide was obtained throughout the course of the oxidation (twenty-four hours), and carbonyldicarbamide, oxidised under similar conditions, was not entirely converted into cyanuric acid even after forty-eight hours. These facts indicate that the oxidation of uric acid by hydrogen peroxide at low temperatures and high excess of alkali is fundamentally different from that occurring at high temperatures and a low concentration of alkali, and that some intermediate product must exist in the alkaline solution after oxidation, which is decomposed during the acidification, constituting the first step in the analysis of the products. To test this point, the alkaline solution resulting from the oxidation was treated with manganese dioxide to destroy the excess of hydrogen peroxide, and was then neutralised by acetic acid, whereby a 60% yield of a mixture of the normal and the acid salts of a dibasic acid,  $C_4H_3O_5N_3$ , [ammonium salt,  $C_4H_3O_5N_3(NH_4)_2$ ], was obtained. This acid, oxidised in acid solution by hydrogen peroxide, gives an 80% yield of cyanuric acid; it cannot be converted into allantoin, carbonyldicarbamide, or uroxic acid (see also next abstract).

The formation of cyanuric acid is in all cases a secondary reaction. It may be formed by the alkaline oxidation of allantoin, especially in neutral solution at high temperature, by the action of alkali alone on carbonyldicarbamide, and, in the best yield, from the acid,  $C_4H_3O_5N_3$ , as above.

Attempts to trace a parallelism between the oxidising action of hydrogen peroxide and of potassium permanganate on uric acid have been unsuccessful.

C. S.

**Hydrogen Peroxide as a Reagent in the Purine Group.**  
**III. Allantoxanic Acid as an Oxidation Product of Uric Acid.** F. J. MOORE and RUTH M. THOMAS (*J. Amer. Chem. Soc.*, 1918, **40**, 1120—1132. Compare preceding abstract).—The best conditions for preparing Venable's acid,  $C_4H_3O_5N_3$ , are the oxidation by hydrogen peroxide at the ordinary temperature of an alkaline solution of uric acid, the excess alkalinity of which is approximately normal. The ammonium salt when heated in a sealed tube at  $150^\circ$  is converted almost quantitatively into ammonium carbonate and allantoxaidine, the latter also being formed when the barium salt is treated with a slight excess of

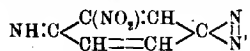
sulphuric acid and the filtrate is evaporated. This suggests that Venable's acid is hydrated allantoxanic acid,  $C_4H_5O_4N_3 \cdot H_2O$ , and the suggestion is confirmed by the identity of its ammonium salt with ammonium allantoxanate prepared by Ponomarev's method and by its reduction to hydroxonic (dihydroallantoxanic) acid by sodium amalgam.

In the formation of allantoxanic acid from uric acid by hydrogen peroxide, neither allantoin nor glycol-uril is an intermediate product. The oxidation of allantoxanic acid to cyanuric acid by hydrogen peroxide in acid solution does not pass through allantoxidine.

C. S.

**Acetyl-*p*-diazoidimides Derived from Substituted *p*-Phenylenediamines.** GILBERT T. MORGAN and DAVID ALEXANDER CLEAGE (T., 1918, 113, 588—596).—The general nature of the reaction by which acyl-*p*-diamines can be converted into acyl-*p*-diazoidimides, although indicating the considerable influence of the acyl group on the intramolecular condensation, nevertheless does not preclude the possibility of isolating the parent substances of this series of diazo-compounds. Derivatives of *p*-phenylenediamine containing acidic substituents in the nucleus have therefore been submitted to examination.

2-Nitro-*p*-phenylenediamine in dry acetone reacts with nitrous anhydride, yielding 3-nitro-*p*-phenylene-1-diazo-4-imide,



a brown, crystalline solid which becomes resinous when warmed to the ordinary temperature. The acetyl derivative of this substance, brownish-red plates, which explode at  $140^\circ$ , combines with  $\beta$ -naphthol, with formation of 3-nitro-4-acetylaminobenzeneazo- $\beta$ -naphthol,  $NHAc \cdot C_6H_3(NO_2) \cdot N_2 \cdot C_{10}H_7 \cdot OH$ , a dark red powder, m. p. above  $290^\circ$ ; this substance on hydrolysis gives 3-nitro-4-aminobenzeneazo- $\beta$ -naphthol, a pale brown powder, m. p.  $208^\circ$ , which after further diazotisation reacts with  $\beta$ -naphthol, producing a bisazo-derivative, and with hot alcohol producing 3-nitrobenzeneazo- $\beta$ -naphthol, orange crystals, m. p.  $192^\circ$ . The identity of the last substance, which serves to confirm the constitution ascribed to the above nitroacetylphenylenediazoidimide, is demonstrated by direct comparison with a specimen synthesised from *m*-nitroaniline. Further evidence as to the constitution is adduced by the preparation of the isomeric 2-nitro-4-acetyl-*p*-phenylene-1-diazo-4-imide,  $C_6H_4O_3N_4$ , decomp.  $142^\circ$  (with explosion), by the interaction of 2-nitro-4-acetyl-*p*-phenylenediamine and nitrous anhydride in dry acetone; this combines with  $\beta$ -naphthol, giving rise to 2-nitro-4-acetylaminobenzeneazo- $\beta$ -naphthol, a red substance, m. p.  $298^\circ$ , the hydrolysis of which yields 2-nitro-4-aminobenzeneazo- $\beta$ -naphthol. By further diazotisation, this product can be made to combine again with  $\beta$ -naphthol, giving a bisazo-compound, and also to undergo reduction by hot alcohol to 2-nitrobenzeneazo- $\beta$ -naphthol, the

identity of which is also confirmed by direct comparison with a specimen prepared from *o*-nitroaniline.

In a similar manner, 2:6-dichloro-*p*-phenylenediamine is found to react with nitrous anhydride in dry acetone, giving unstable 3:5-dichloro-*p*-phenylene-1-diazo-4-imide, which yields a more stable 4-acetyl derivative, a grey, crystalline powder, decomp. 132° with explosion. This acetyl derivative gives colour reactions with the naphthols and naphthylamines identical with those exhibited by the yellow 3:5-dichloro-4-acetyl-*p*-phenylene-1-diazo-4-imide, decomp. at 133°, obtained by diazotising 2:6-dichloro-1-acetyl-*p*-phenylenediamine, and the suggestion is made that the almost colourless and yellow forms of the acetyl compound may be represented by the cyclic diazoimide constitution,  $C_6H_2Cl_2 \begin{smallmatrix} NAc \\ \diagdown \\ N_2 \end{smallmatrix}$ , and

the diazoquinoneimide constitution,  $NAc:C_6H_2Cl_2 \begin{smallmatrix} N \\ \diagdown \\ N \end{smallmatrix}$  respectively.

the difference disappearing on combination with phenols or bases. 2:6-Dichloro-4-acetyl-*p*-phenylene-1-diazo-4-imide,  $C_6H_3ON_2Cl_2$ , almost colourless plates, decomp. at 138°, obtained from 2:6-dichloro-4-acetyl-*p*-phenylenediamine, is to be regarded as probably of cyclic diazoimide structure. D. F. T.

**Compounds Derived from Proteins by Energetic Treatment with Nitric Acid.** F. KNOOP (*Zeitsch. physiol. Chem.*, 1918, 101, 210—211. Compare Mörner, this vol., i, 198).—The unidentified acid substances discovered by Mörner (*loc. cit.*) amongst the oxidation products of protein are probably 5-nitro-glyoxaline-4-carboxylic acid,  $C_4H_3O_4N_3$  (Windaus and Öpitz, A., 1911, i, 752), and glyoxaline-4-glyoxylic acid,  $C_5H_4O_3N_2$  (Knoop, A., 1907, i, 788). Both substances are oxidation derivatives of histidine and have the properties described by Mörner. Attention is directed to the fact that the latter substance,  $C_5H_4O_3N_2$ , must contain either 2 or 4 atoms of hydrogen instead of 3 (as found by Mörner) if it consists of a simple molecule. H. W. B.

**Preparation of Ovalbumin, and its Refractive Indices in Solution.** A. R. C. HAAS (*J. Biol. Chem.*, 1918, 35, 119—125).—The crystallisation of ovalbumin is found to be dependent on the hydrogen ion concentration of the globulin-free solution of white of egg; crystals are formed in the presence of ammonium sulphate when the hydrogen ion concentration lies between  $10^{-5}$  and  $10^{-6}$ .

The refractive indices of solutions of ovalbumin in water, 1% ammonium sulphate, and in various concentrations of sodium hydroxide obey the law  $n - n_1 = a \times c$ , where  $n$  is the observed refractive index of the protein solution,  $n_1$  that of the solvent,  $c$  the percentage of dissolved protein, and  $a$  a constant, which is found to be  $0.00177 \pm 0.00006$ . The corresponding constant for the albumins of ox serum is  $0.00177 \pm 0.00008$  (Robertson, A., 1912, ii, 611).

H. W. B.

**Preparation of Pure Caseinogen.** LUCIUS L. VAN SLYKE and JOHN C. BAKER (*J. Biol. Chem.*, 1918, **35**, 127—136).—The caseinogen is prepared from undiluted milk by treatment with normal acid, preferably lactic or a mixture of 1 part of hydrochloric and 2 parts of acetic acid. The acid is introduced slowly into the milk below the surface, the tip of the tube carrying the acid being so arranged that it is very close to a mechanical stirrer revolving at a high speed and also near the bottom of the vessel containing the milk. Under these conditions, the acid does not cause coagulation of the caseinogen at the point where the acid first comes into contact with the milk.

The product, the preparation of which requires only about ten hours, is a fine, white powder containing 0.10% of ash and 0.80% of phosphorus. It is free from inorganic phosphorus, calcium, and hydrolytic products of protein, and dissolves at once in dilute solutions of monoacidic alkalis to a clear solution. H. W. B.

**Constitution of the True Nucleic Acids.** R. FEULGEN (*Zeitsch. physiol. Chem.*, 1918, **101**, 288—295. Compare this vol., i, 85, and Levene and Jacobs, A., 1912, i, 926).—A theoretical paper in which the general arrangement of the nucleotides in nucleic acid suggested by Levene is accepted, although the precise method of linking together of the nucleotides is regarded as unsettled (compare also Jones and Read, A., 1917, i, 232, 233).

H. W. B.

**Preparation and Properties of Thymic Acid.** R. FEULGEN (*Zeitsch. physiol. Chem.*, 1918, **101**, 296—309).—Thymic acid is prepared by treating sodium nucleinate with a slight excess of sulphuric acid and keeping the mixture for forty minutes at 80°. The acid is separated in the form of its barium salt, and on hydrolysis yields cytosine and thymine.

H. W. B.

**Influence of Normal Salts, Bases, and Acids on the Precipitability of Gelatin by Alcohol.** JACQUES LOEB (*J. Biol. Chem.*, 1918, **34**, 489—501. Compare this vol., i, 240).—In these experiments, finely powdered gelatin is treated for an hour with solutions of normal salts, bases, or acids of various concentrations; the excess of the solution is in each case washed away with water, a 1% solution of the washed gelatin in water being then prepared and treated with alcohol until precipitation just occurs. It is found that when the concentration of the salt solution exceeds a certain limit, which is about  $M/128$  in the case of normal salts with univalent anions and cations and monoacidic bases, the gelatin becomes non-precipitable by alcohol, whilst in the case of normal salts with bivalent anion and univalent cation, and also in the case of strong monobasic acids, the concentration at which non-precipitability occurs is just twice as great, namely,  $M/256$ . After treatment with solutions of normal salts with bivalent cations and univalent or bivalent anions, the gelatin remains precipitable



with alcohol for all the concentrations of the salt used. These experiments confirm the conclusions previously drawn by the author in former papers (*loc. cit.*). H. W. B.

**Action of Pancreatic Enzymes on Casein.** H. C. SHERMAN and DORA E. NEUN (*J. Amer. Chem. Soc.*, 1918, **40**, 1138—1145).

—A comparative study of the hydrolysis of casein by various preparations derived from the pancreas. Extraction of high-grade commercial pancreatin with 50% alcohol leaves a residue having about the same proteolytic activity as the original pancreatin. The "sac precipitate" which settles out of the amylase solution during the dialysis in 50% alcohol preceding the final precipitation of the amylase preparation (Sherman and Schlesinger, A., 1912, i, 815; 1915, i, 604) has fifteen times the proteolytic activity of the original pancreatin and about four times that of the most active commercial trypsin. The final preparation of pancreatic amylase, purified as described previously (*loc. cit.*), has proteolytic activity fully as great as that of high-grade trypsin. C. S.

**Enzyme Chemistry.** H. VON EULER (*Zeitsch. Elektrochem.*, 1918, **24**, 173—177).—In the inversion of sucrose by yeast, it is shown that the invertase increases to a maximum and the formation of the enzyme follows the formula  $dx/dt=k(a-x)$ . Other experiments on the hydrolysis of starch by the enzyme of *Mucor mucedo* are described; in this case, the velocity of the formation of the enzyme is constant. J. F. S.

**The Law of Action of Sucrase.** H. COLIN and (MILLER) A. CHAUDON (*Compt. rend.*, 1918, **167**, 208—210).—The inversion of sucrose by sucrase does not obey Wilhelmy's law,  $x=a(1-e^{-kt})$ , at concentrations of sucrose exceeding 2% or 3%, but there is probably a definite ratio of sucrose to sucrase below which the law holds good. Using 5 c.c. of a very active sucrase preparation, the authors have obtained results in agreement with the law up to concentrations of 2% of sucrose. W. G.

**Chemical Reaction in the System: Urea-Urease.** ENCHI YAMAZAKI (*J. Tokyo Chem. Soc.*, 1918, **39**, 125—184).—Ammonium carbamate has always been found by Fenton's method in the product of the action of urease on urea. It may therefore be presumed that the decomposing action of urease is a successive hydrolysis of urea,  $\text{NH}_2\text{CO}\cdot\text{NH}_2 \rightarrow \text{NH}_2\text{CO}_2\cdot\text{NH}_4 \rightarrow (\text{NH}_4)_2\text{CO}_3$ , in opposition to the view of the formation of an intermediate product of urea and urease.

The experiments were always carried out in a slightly acidic solution obtained by saturating the reacting system with carbon dioxide. Notwithstanding the phase difference of the two constituents of the reaction, it seems to be a homogeneous chemical reaction, because stirring has no effect on its velocity. The velocity constant  $k_1$  of the first hydrolysis was determined by the initial

velocity, and the constant  $k_2$  of the second hydrolysis by some trials. With a 0.02*N*-solution of urea and a solution of urease containing 0.2 gram in 100 c.c., the values obtained were  $k_1=0.0068$ ,  $k_2=0.00617$  at 25°. These constants vary proportionately to the concentration of the urease. A good coincidence was obtained between the observed values for the velocity of the reaction and the values for  $k_1$  and  $k_2$  calculated by the formula derived from Rakowski's general theory of unimolecular successive chemical reactions (A., 1907, ii, 74). The temperature coefficient of this reaction is 2 per 10° between 15° and 35°. Many reagents are adsorbed by urease and show a poisonous action; the action of alkali hydroxide is reversible, whilst that with hydrochloric acid, mercuric chloride, or silver sulphate is irreversible. S. H.

**Synthesis of Organic Sodium Derivatives.** ANTONIO MADINAVEITIA and JOSÉ RANERO (*Anal. Fis. Quim.*, 1918, 16, 142—145).—Dimethylaniline reacts with mercuric acetate to form dimethylaniline mercury acetate,  $\text{Me}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{Hg}\cdot\text{CO}_2\text{Me}$ , which is transformed by sodium hyposulphite into mercury *pp*-tetramethyldiaminodiphenyl,  $(\text{Me}_2\text{N}\cdot\text{C}_6\text{H}_4)_2\text{Hg}$ . The solution of this substance in benzene reacts with sodium, the mercury being replaced by the alkali metal. The mechanism of the process is similar to the formation of sodium phenyl by the interaction of sodium and mercury phenyl. The sodium compound is spontaneously inflammable on contact with air. A. J. W.

**Simplified Method for the Preparation of Tin Triaryl Haloids.** ERICH KRAUSE (*Ber.*, 1918, 51, 912—914).—If the tin tetra-aryls are brominated in ordinary organic media, or alone, no matter how carefully the conditions are controlled, the main products are the tin diaryl dibromides. If the compounds are suspended in pyridine chilled by means of solid carbon dioxide, however, bromination can be stopped at the first stage. The product is freed from solvent and bromobenzene (or analogous compound) by distillation, then transferred to ether, and shaken with 30% sodium hydroxide. The tin triaryl hydroxide dissolves in ether, and can be converted into any desired haloid by means of the acids.

Tin triphenyl chloride,  $\text{SnPh}_3\text{Cl}$ , m. p. 106°, b. p. 240°/13.5 mm. (compare Aronheim, A., 1879, 250, 651), *bromide*, fern-like groups of octahedra, m. p. 120.5°, b. p. 249°/13.5 mm., and *iodide*, large, snow-white, quadratic, monoclinic prisms, m. p. 121°, b. p. 253°/13.5 mm., have been prepared in this way in yields amounting to 90—95%. J. C. W.

### Physiological Chemistry.

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**Comparative Study of the Influence of Carbohydrates and Fats on the Nutritive Power of Alimentary Proteins.** F. MAIGNON (*Compt. rend.*, 1918, 167, 172—175. Compare this vol., i, 359).—Feeding experiments with rats, using diets of egg-albumin and fat, or egg-albumin and starch, or a mixture of the three, indicate that the albumin is better utilised with the fat than with starch, and that the minimum of albumin necessary is much lower with fat than with starch. The most satisfactory mixture of albumin and fat is in the proportion 1:1, even if starch is present.  
W. G.

**The Nutritive Equilibrium of the Animal Organism.** JULES AMAR (*Compt. rend.*, 1918, 167, 241—242).—The author points out that Maignon's results for fat and starch as supplements to protein in feeding rats (compare preceding abstract) are in opposition to those of Atwater and Benedict (compare A., 1903, ii, 308) and Mendel and Lewis (A., 1913, i, 1406). He directs attention to his own work in this connexion (compare *Moteur humain*, 1909, 289).  
W. G.

**Nitrogenous Metabolism of the Central Nervous System.** ELSE HIRSCHBERG and HANS WINTERSTEIN (*Zeitsch. physiol. Chem.*, 1918, 101, 212—222. Compare this vol., i, 52).—The isolated spinal cord of the frog contains in the fresh material 1.30% of nitrogen, and 1.25% in cords freed from the outer membranes. The content of nitrogen is unaltered by preservation of the cords in air or oxygen, but falls rapidly when immersed in oxygenated saline solution. The addition of a trace of a calcium salt to the saline solution increases the rate of loss of nitrogen from the cord; potassium salts decrease it. Treatment with 4% of alcohol practically arrests nitrogenous metabolism; electrical stimulation increases it nearly fourfold. The katabolic action is an oxidative one, because it fails to occur in the absence of free oxygen.  
H. W. B.

**Utilisation of various Saccharides in the Metabolism of the Central Nervous System.** ELSE HIRSCHBERG (*Zeitsch. physiol. Chem.*, 1918, 101, 243—254. Compare Hirschberg and Winterstein, this vol., i, 52).—Maltose and sucrose are not utilisable for the maintenance of the metabolic processes of the surviving spinal cords of frogs. Dextrose and levulose have about equal power in maintaining metabolism in the resting state, whilst lactose has less and galactose considerably more, probably due to the participation of the latter substance in the composition of nervous tissue. During excitation, the consumption of dextrose by the tissue greatly exceeds that of any other saccharide other than

galactose. Dextrose is therefore the best material to supply for the rapid production of power for the use of nervous tissues.

H. W. B.

**Oxidation Catalysts in the Animal Organism. Action of certain Ferments on Oxydones.** LEOPOLDO LÓPEZ PEREZ (*Anal. Fis. Quim.*, 1918, 16, 397—421).—A full account of work of which a preliminary note has appeared (see this vol., i, 88).

**Origin of Creatine. III.** L. BAUMANN and H. M. HINES (*J. Biol. Chem.*, 1918, 35, 75—82).—Perfusion of dog muscle with choline or sarcosine leads apparently to the production of creatine. Arginine, histidine, betaine, methylguanidine, and cyanamide when similarly treated do not yield any notable increase in the amount of creatine in muscle or urine.

H. W. B.

**Amino-acids of Mature Human Placenta.** VICTOR JOHN HARDING and CHARLES ATHERTON FORT (*J. Biol. Chem.*, 1918, 35, 29—41).—The amount of arginine in human placenta is twice as much as that present in any other human organ (liver, heart, kidney, muscle).

H. W. B.

**Caseinogen of Human Milk.** A. W. BOSWORTH and LOUISE A. GIBLIN (*J. Biol. Chem.*, 1918, 35, 115—117).—Caseinogen prepared from human milk resembles the caseinogen prepared from cows' and goats' milk in the following respects: It has the same nitrogen, phosphorus, and sulphur content, the same molecular weight and degree of valency; it gives the same series of salts with bases; it is acted on by rennin in the same manner, producing the same casein.

H. W. B.

**Free Lactic Acid in Sour Milk.** LUCIUS L. VAN SLYKE and JOHN C. BAKER (*J. Biol. Chem.*, 1918, 35, 147—178).—Lactic acid exists in sour milk largely as lactate, but partly as free acid, some of the latter being in solution, whilst a smaller part is adsorbed by the caseinogen or casein. Sterilised milk inoculated with *Bacterium lactis acidii* does not show the presence of free lactic acid until about twenty hours after the inoculation; the amount then rapidly increases and reaches about 20 c.c. of 0.1*N*-acid in forty-eight hours. The  $p_H$  value changes from 6.5 in fresh milk to 4.17 in forty-eight hours. The caseinogen begins to coagulate when the  $p_H$  reaches 4.64 to 4.78. During the coagulation process, the hydrogen-ion concentration remains constant, although the acidity by titration increases slightly. About 20% of the free lactic acid in coagulated sour milk is adsorbed by the casein.

The first perceptible sign of souring in milk is a characteristic flavour, discernible to the senses of both taste and smell, due to the presence of a volatile compound formed in the souring process, and not to lactic acid. There does not appear to be any relation between either hydrogen-ion concentration or acidity by titration and the first sign of this flavour.

Various methods are described for estimating the free lactic acid and of that portion of it which is adsorbed by the caseinogen or casein.

H. W. B.

**Glycerides of Butter Fat.** CONRAD AMBERGER (*Zeitsch. Nahr. Genussm.*, 1918, **35**, 313—381).—Butter fat contains only a small quantity (2.4%) of triolein, the greater part of the oleic acid existing in the fat in the form of mixed glycerides. If the oleic acid is present as triolein, the fat when hydrogenised should yield a corresponding quantity of tristearin, but such is not found to be the case. Butyric and other volatile acids are also present in the fat as mixed glycerides; tributyrin cannot be isolated. Examination of the alcohol-soluble portion of hydrogenised butter fat shows that the original fat contains butyrodiolein, butyropalmitolein, and oleodipalmitin. The author has also isolated from butter fat a glyceride, m. p. 67.9°, and yielding mixed fatty acids, m. p. 55.5°.

W. P. S.

**Transformation of Tetrahydronaphthalene (Tetralin) in the Animal Body.** G. SCHROETER and K. THOMAS (*Zeitsch. physiol. Chem.*, 1918, **101**, 262—275).—Tetrahydronaphthalene fed to a dog is absorbed and eventually excreted in combination with urea. The existence of four compounds of tetrahydronaphthalene and carbamide is theoretically possible, and the authors have succeeded in preparing all of them by the interaction of potassium cyanate on the respective amines in aqueous solution. *ar-Tetrahydro- $\alpha$ -carbamidonaphthalene*,  $C_{11}H_{14}ON_2$ , crystallises in square plates from alcohol, softens at 198°, and melts at about 206° (quickly heated, at 212°); *ar-tetrahydro- $\beta$ -carbamidonaphthalene*, needles from water, m. p. 134° (decomp.); *ac-tetrahydro- $\alpha$ -carbamidonaphthalene*, needles, m. p. 210.5°; *ac-tetrahydro- $\beta$ -carbamidonaphthalene*, needles, m. p. 183°. Comparison of the natural product with these compounds shows that tetralin in its passage through the body is converted into *dl-ac-tetrahydro- $\alpha$ -carbamidonaphthalene*.

In the preparation of the *ar- $\beta$* -compound, a small amount of a substance was obtained in the form of colourless needles, which did not melt below 245° and possessed the composition of *di-ar-tetrahydro- $\beta$ -naphthylcarbamide*,  $(C_{10}H_{12}N)_2CO$ .

H. W. B.

**Relation between the Chemical Structure of the Opium Alkaloids and their Physiological Action on Smooth Muscle with a Pharmacological and Therapeutic Study of some Benzyl Esters.** I. Relation of the Chemical Structure of the Opium Alkaloids to their Action on Smooth Muscle. DAVID I. MACHT (*J. Pharm. Expt. Ther.*, 1918, **11**, 389—417).—The results indicate that in respect to their physiological action on the rhythmic contraction and tonicity of smooth muscle from various organs, the opium alkaloids can be divided into two classes: (1) the morphine group; (2) the papaverine group. Members of

the first group, containing a pyridine-phenanthrene nucleus, exert a stimulating action which appears to be associated with the pyridine or piperidine component of the molecule, whilst the members of the papaverine or benzylisoquinoline group exert an inhibitory action which can be traced to the benzyl radicle. Alkaloids such as benzylmorphine or peronine, containing both significant groupings, have an anomalous action on smooth muscle.

H. W. B.

**Pharmacology of the Vitamines.** FR. UHLMANN (*Zeitsch. Biol.*, 1918, **68**, 419—456).—The administration of vitamins to cats and dogs, either subcutaneously, intravenously, or by the mouth, causes a marked stimulation of the salivary, sweat, gastric, and other glands which is inhibited by atropine. The author considers that the vitamins in the food play an essential part in the processes of digestion and metabolism through their stimulatory action on glands producing external and internal secretions. The commercial vitamin preparation "orypan," obtained from rice husks, was chiefly employed, but similar results were given in some experiments by extracts of oats, meat, yeast, etc.

H. W. B.

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## Chemistry of Vegetable Physiology and Agriculture.

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### Occurrence of Methylpentosans in Cereals and Legumes.

KINTARŌ ŌSHIMA and KINSUKE KONDŌ (*J. Tokyo Chem. Soc.*, 1918, **39**, 294—300).—On account of incompleteness of the method of determination of methylpentosans, there has been doubt as to their occurrence in some seeds in which they have been reported to exist. The authors have therefore examined certain cereals and legumes by their improved method (this vol., ii, 338), and have found methylpentosans in all varieties of the soja bean, whilst it is absent in the cereals investigated.

S. H.

### Phytochemistry of the Crowberry (*Empetrum nigrum*).

L. VAN ITALLIE (*Pharm. Weekblad*, 1918, **55**, 709—717).—The leaves of *Empetrum nigrum* contain a wax composed wholly, or in great measure, of ceryl cerotate, benzoic acid, urson, tannin, dextrose, and probably rutin. The anhydrous urson has the formula  $C_{10}H_{16}O$ , and is identical with the derivative obtained from the leaves of *Uva Ursi*.

*Empetrum nigrum* contains no alkaloids, andromedotoxins, or glucosides decomposed by emulsin. The presence of benzoic acid and urson points to a probable relationship between the *Empetraceæ* and *Eriaceæ*.

A. J. W.

**Plant Sterols. I. Sterol Content of Wheat (*Triticum sativum*).** MARY TAYLOR ELLIS (*Biochem. J.*, 1918, **12**, 160—172).—The chief phytosterol present in the wheat grain is sitosterol. The embryo also contains sitosterol, but the phytosterol in the bran differs in its properties from sitosterol. The unsaponifiable ether extract of the vegetative organs, leaves, stems, etc., contains a phytosterol, together with an alcohol,  $C_{20}H_{42}O$ , crystallising from ethyl acetate and acetone in granular lumps of small crystals, m. p.  $83^{\circ}$ ; acetate, m. p.  $65^{\circ}$ ; it does not give the cholesterol colour reactions.

The amount of phytosterol in normal wheat plants is greater than that which was present in the grain from which the plants were grown; in etiolated plants, an increase in the phytosterol content as compared with the grain is not perceptible. It is suggested that the sterols form an essential part of cell membranes.

H. W. B.

**Plant Sterols. II. Occurrence of Phytosterol in some of the Lower Plants.** MARY TAYLOR ELLIS (*Biochem. J.*, 1918, **12**, 173—177).—Ergosterol and fongisterol occur in the fungus *Polyporus nigricans*, and probably also in *P. betulinus*. Sterols may also be detected in *Laminaria*, *Sphagnum*, *Agaricus rubescens*, and *Lactarius subdulcis*.

H. W. B.

**Some Poisonous Plants in the Order Solanaceæ. II. Nicotiana suaveolens.** J. M. PETRIE (*Proc. Linn. Soc. N.S. Wales*, 1916, **41**, 148—151; from *Physiol. Abstr.*, 1918, **3**, 199).—This plant contains nicotine.

S. B. S.

**The Production of Anthocyanins and Anthocyanidins. III.** ARTHUR ERNEST EVEREST (*Proc. Roy. Soc., [B]*, 90, 251—265, Compare A., 1914, i, 978; 1915, i, 25).—The author has isolated the anthocyanin pigment from the purplish-black viola, "Black Knight," petals, and has shown that it is a delphinidin glucoside and identical with the violanin obtained by Willstätter and Weil from the bluish-black pansy (compare *Annalen*, 1916, **412**, 178). An examination of the alum reaction as described by Willstätter and his collaborators shows that the colour reactions of anthocyanins, described as due to alum, are really due to the presence of iron as an impurity in the alum, and are not obtained if the reagent is pure.

An examination of the yellow sap pigment from the same violas shows that it contains a myricetin glucoside (or less probably a gossypetin glucoside) and also another yellow sap pigment which does not give a green coloration with dilute alkalis. Thus the presence in one flower of an anthocyanin pigment and of the flavonoid derivatives from which it would be produced by reduction is shown for the first time.

W. G.

## General and Physical Chemistry.

**The Scattering of Light in Hydrogen, Oxygen, and Nitrogen.** M. BORN (*Ber. Deut. physikal. Ges.*, 1918, 20, 16—32).

—In a previous paper (*ibid.*, 1917, 19, 243), the author has shown that gases which consist of anisotropic molecules exhibit a scattering effect other than that which has been explained by Rayleigh's theory. The rays which characterise this new type of opalescence are in part non-polarised, and can accordingly be sharply distinguished from the polarised rays which are associated with the more familiar scattering effect. Experiments made by Smoluchowski on hydrogen, oxygen, and nitrogen afforded no evidence of the existence of the effect predicted by the author, and it is supposed that this may be due either to the insufficient anisotropy of the molecules or to the lack of precision in the method of observation.

By reference to the molecular models which have been recently suggested for hydrogen, oxygen, and nitrogen, the author has calculated the magnitude of the effects to be expected, and finds that, although small, it should be possible to observe the scattering effects in question in the case of each of these gases with a suitably designed arrangement of apparatus. H. M. D.

**Refractivities of Saturated and Unsaturated Compounds.**

GERVAISE LE BAS (*Trans. Faraday Soc.*, 1918, 13, 414—419. Compare this vol., ii, 49).—From a comparison of the molecular refractivities of corresponding derivatives of benzene and of the saturated cyclic hydrocarbons, it is found that the augmentations due to substitution in the benzene ring are considerably greater than those which accompany substitution in rings of the polymethylene series. In this connexion, it may be noted that the unsubstituted saturated cyclic hydrocarbons show no anomaly in refractive power, whether the ring system is simple or complex.

H. M. D.

**Ketonic and Enolic Modifications of Compounds.**

GERVAISE LE BAS (*Trans. Faraday Soc.*, 1918, 13, 420—423).—The constitution of various keto-enol tautomerides is considered in relation to their refractivities. The molecular refractivities of acetylacetone, methylacetylacetone, ethyl oxaloacetate, ethyl mesityloxido-oxalate, methyl cyanoacetoacetate, ethyl acetylmalonate, ethyl acetone-lincarboxylate, and ethyl  $\beta$ -hydroxy- $\alpha$ -phenylacrylate and its acetate lead to the conclusion that these substances exist in one form only, and that the different isomerides appear to be mutually exclusive.

H. M. D.

**Presence in the Solar Spectrum of the Water Vapour Band  $\lambda$  3064.** A. FOWLER (*Proc. Roy. Soc.*, 1918, [A], 94, 472—475).

A comparison is made of the lines composing the band  $\lambda$  3064,



which is always obtained in the spectra of gases containing both hydrogen and oxygen, with the lines of the solar spectrum in this region as plotted and measured by Rowland. It is shown that, despite the interference of certain metallic lines, this band is also present in the solar spectrum. J. F. S.

**The Ultra-violet Band of Ammonia and its Occurrence in the Solar Spectrum.** A. FOWLER and C. C. L. GREGORY (*Proc. Roy. Soc.*, 1918, [A], **94**, 470—471).—Photographs of the ammonia spectrum have been made by burning a copper arc in an atmosphere of ammonia. From these, it is shown that the ammonia spectrum consists of a main band, which is made up of a bright central maximum at  $\lambda$  3360, a secondary maximum at  $\lambda$  3371, and a number of lines, arranged in groups of three, which extend to a considerable distance in both directions. The lines composing the maxima are very closely crowded, and are found to be arranged in series of ordinary type. The components of the groups of three are widely separated near the central maximum, but the intervals rapidly diminish, and there is finally coalescence at  $\lambda$  3450 towards the red and at  $\lambda$  3287 towards the violet, where the lines fade out. This spectrum has been compared with the *P*-group of the solar spectrum, and shown to be practically identical; hence the presence of ammonia in the absorbing atmosphere of the sun is definitely established. J. F. S.

**The Ultra-red Absorption Spectrum of Water Vapour.** GERHARD HETTNER (*Ann. Physik*, 1918, [iv], **55**, 476—496).—Measurements of the absorption of ultra-red rays by water vapour have been made for the region extending from the visible spectrum to a wave-length of  $34\mu$ . An improved arrangement of apparatus for the investigation of absorption in the long-waved region is described. The results recorded show the existence of 78 maxima, of which only 20 have been recorded by previous observers. The wave-lengths of the maxima are tabulated, and a curve is given which shows the absorption relations in detail. H. M. D.

**Characteristic Ultra-red Vibrations of Nitrates.** CLEMENS SCHAEFER and MARTHA SCHUBERT (*Ann. Physik*, 1918, [iv], **55**, 577—588).—The reflection spectra of sodium nitrate, potassium nitrate, rubidium nitrate, lead nitrate, barium nitrate, and mercurous nitrate have been determined with polarised light and ordinary light. All six substances show three maxima, at approximately  $7.5\mu$ ,  $12.5\mu$ , and  $15.0\mu$ ; in addition, mercurous nitrate shows a fourth maximum at  $10.08\mu$  with ordinary light. From the examination with polarised light, it is shown for the biaxial nitrates that the three maxima observed with ordinary light are made up of three components corresponding respectively with the vibrations parallel to the axes of the three indices of refraction. The characteristic vibrations, as in the case of the carbonates and sulphates (*A.*, 1916, ii, 506), depend very slightly on the

metal and are due to internal vibrations of the  $\text{NO}_3$  group, which are practically the same in all the nitrates examined. The similarity between the space gratings of sodium nitrate and calcium carbonate, as put forward by Bragg, is discussed in the light of abnormalities found in the present work. J. F. S.

**The Distribution of Intensity in Series Spectra Excited by Cathode Rays.** J. HOLTSMARK (*Ann. Physik*, 1918, [iv], 55, 245—298).—The fact that previous attempts to measure the changes in the distribution of the intensity in series lines under the influence of varying conditions have not led to consistent results is attributed to errors introduced by the method of excitation. New experiments have been made on the Balmer series with cathode rays as the exciting agent, and the results indicate that the relative intensities of the series lines are, in these circumstances, independent of the current strength and also of the fall of potential. On the other hand, it is found that the lines of longer wave-length become relatively more intense as the pressure of the hydrogen increases. The connexion between the pressure  $p$  and the ratio  $K$  of the intensities of the lines  $H_\beta$  and  $H_\gamma$  is expressed by the equation  $Kp^{-0.125} = \text{constant}$ . The pressure effect is not obtained when the increase of pressure is brought about by the addition of another gas to the hydrogen. Experiments in which the hydrogen was mixed with iodine, oxygen, argon, and helium respectively, all gave negative results in that these gases produced no change in the relative intensities of  $H_\beta$  and  $H_\gamma$ . On the other hand, observations made on the series lines of helium at different pressures showed a pressure effect similar to that found in the case of hydrogen.

The theoretical interpretation of the pressure effect is discussed, and the author concludes that Bohr's hypothesis relative to the origin of the effect is not in agreement with the observations.

H. M. D.

**Electron Theory of the Natural Optical Rotatory Power of Isotropic and Anisotropic Liquids.** M. BORN (*Ann. Physik*, 1918, [iv], 55, 177—240).—A theoretical paper in which the author's previous attempts (compare A., 1915, ii, 659) to explain the natural rotatory power of optically active substances on a molecular basis in terms of electrons are more completely developed. The general formulæ derived are discussed in reference to the nature of the molecular forces and the symmetry relations, and are applied to the consideration of isotropic liquids with natural rotatory power, of liquids rendered anisotropic by means of an electric field, and of liquids which are normally anisotropic (liquid crystals).

H. M. D.

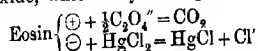
**Colour Determination of Faint Luminescence.** HARRY B. WEISER (*J. Physical Chem.*, 1918, 22, 439—449).—A method of determining the colour of faint luminescence is described which

consists in photographing the luminescence on a panchromatic plate and interposing a series of colour screens between the source of light and the plate. The method may be used in all cases when the glow is uniform and sufficiently strong to affect a highly sensitive photographic plate.

The results obtained in the investigation of the chemiluminescence emitted in the oxidation of alkaline pyrogallol by hydrogen peroxide, of phosphorus in acetic acid solution by hydrogen peroxide, and of amarine in alkaline alcoholic solution by hydrogen peroxide, are described in detail. The crystalline chlorine and bromine, are described in detail. The chemiluminescence emitted when a saturated aqueous solution of sodium chloride is mixed with alcohol or hydrochloric acid was also examined, with the result that the colour of the light is shown to be bluish-violet.

H. M. D.

**Photolysis and Electrolysis.** EMIL BAUR (*Helvetica Chim. Acta*, 1918, 1, 186—201).—A theoretical paper in which the author evolves an electrolytic theory to explain the mechanism of photolysis. A substance which has been subjected to light has set up a molecular potential difference, and as such is capable of effecting a chemical reaction. Photolysis is therefore to be regarded as molecular electrolysis. Thus the decomposition of Eders's solution by eosin in light is to be regarded as a cathodic reduction of mercuric chloride to calomel and an anodic oxidation of oxalic acid to carbon dioxide, which may be expressed:



The author then proceeds to calculate the value of the *E.M.F.* operative on the basis of the quantum theory and the assumption that only one energy quantum may be absorbed. The following values are obtained for the lines mentioned: Sodium line,  $\lambda = 589 \mu\mu$ ,  $E = 2.4$  volts; mercury line,  $\lambda = 435 \mu\mu$ ,  $E = 3.2$  volts; Hg (fluorescent line),  $\lambda = 253.6 \mu\mu$ ,  $E = 5.5$  volts; and  $\gamma$ -rays,  $\lambda = 0.012 \mu\mu$ ,  $E = \text{about } 100,000$  volts. A large number of cases are considered in the light of this hypothesis.

J. F. S.

**Absorption of X-Rays.** E. A. OWEN (*Proc. Roy. Soc.*, 1918, [A], 94, 510—524).—According to Bragg and Pierce (*A.*, 1914, ii, 792), the atomic absorption coefficient  $A$  is connected with the atomic number  $N$  of the absorber, and the wave-length  $\lambda$  of the radiation by the equation  $A = CN^4\lambda^{5/2}$ , in which  $C$  is constant over considerable ranges of wave-length, but changes abruptly in the region of selective absorption. From the investigation of the absorption of a large number of aqueous solutions, Aurén (*A.*, 1917, ii, 350) has recently deduced values for the atomic absorption coefficients of the elements which lead to the conclusion that with respect to the magnitude of the absorption coefficient, the elements may be divided into groups, for each of which the atomic absorption coefficient is directly proportional to the atomic number. An attempt is made to account for these discordant results.

The ordinary absorption coefficient is a composite quantity which represents the sum of the fluorescent absorption coefficient and the scattering coefficient. Assuming that the latter has a constant value equal to 0.2, in agreement with the results obtained by Barkla for the light elements and radiation of widely varying wave-length, the author calculates from his observations the values of the atomic fluorescent absorption coefficient, and finds that this is nearly proportional to the fourth power of the atomic number of the absorber. Since it is known that the fluorescent absorption coefficient varies as the cube of the wave-length of the absorbed radiation, the connexion between the atomic fluorescent absorption coefficient  $A_f$ , the atomic number  $N$ , and the wave-length  $\lambda$  may be expressed in the form  $A_f = CN^4\lambda^3$ , where  $C$  remains constant over certain ranges of wave-length, but changes abruptly at critical points. This equation differs from that put forward by Bragg and Pierce in that the coefficient  $A_f$  is independent of the scattering of the radiation and refers only to the loss of energy of X-radiation resulting from the production of corpuscular radiations and the fluorescent X-radiations which accompany them.

The author's measurements were made on zinc, copper, nickel, iron, aluminium, magnesium, water, and filter-paper with radiation of wave-length  $\lambda = 0.586 \times 10^{-8}$  cm. ( $\alpha$ -line of palladium), and the values obtained for the total absorption coefficients agree fairly closely with those recorded by Bragg and Pierce (*loc. cit.*).

It is further shown that, if the scattering coefficient is assumed to have a constant value of 0.2 for all elements from hydrogen to bromine, the equation  $A_f = CN^4\lambda^3$  leads to values for the total absorption which are in close agreement with those obtained in the experiments of Aurén.

H. M. D.

**The Positive Ion as Carrier in the Canal Ray Fluorescence of Inorganic Salts.** SVEN EM. OHLON (*Ber. Deut. physikal. Ges.*, 1918, 20, 9—15).—When inorganic salts are subjected to the action of cathode rays of sufficiently high velocity, the salts fluoresce with the emission of the line spectrum of the metal present in the salt. For different salts of the same metal, the cathode ray energy required for this emissive effect increases with the heat of formation of the salt. The cathode ray energy at which emission begins is found to diminish as the discharge potential increases.

A similar series line emission occurs when inorganic salts are bombarded by canal rays, but the energy of the canal rays required to produce this effect varies to only a small extent when different salts of the same metal are employed, and the variation with magnitude of the discharge potential is also much smaller than in the case of cathode ray bombardment.

The observed differences suggest that the cause of the emission may not be the same in the two cases, and experiments have been devised with the object of elucidating further the changes which occur under the influence of canal rays. In these, the canal rays

were allowed to fall on the powdered salt contained in a small aluminium dish supported in the discharge tube in the path of the canal rays. The dish was connected through a galvanometer to earth, and a small direct-vision spectroscope was focussed on the bombarded salt. The discharge potential was varied, and by taking readings of the galvanometer, it has been found that the emission of the series lines is accompanied by a diminution in the positive current which flows through the galvanometer. This sudden change in the current, which characterises the transition from the non-fluorescent to the fluorescent condition, has been found to occur with salts of sodium, lithium, magnesium, calcium, strontium, barium, cadmium, and copper. The observations afford support for the view that the canal ray fluorescence is due to the metal ions which result from the dissociation of the salt under the influence of the canal rays. The carriers would thus appear to be the same for both cathode ray and canal ray fluorescence.

H. M. D.

**Periods, Atomic Masses, and Electric Charges of the Radioelements.** EMIL KOHLWEILER (*Zeitsch. physikal. Chem.*, 1918, **92**, 685—716).—A theoretical paper in which a number of regularities between the valency, average life, and ray emission of the radioactive elements are put forward. In each disintegration series, those elements which emit  $\alpha$ -rays and have even valencies have longer average lives the greater the atomic mass. Of those pairs of elements which emit  $\alpha$ -rays and have contiguous valencies (that is, IV, V), that with the smaller valency has the greater average life, whether the atomic mass of the pair is the same or not. Of two directly following  $\beta$ -ray changes, the first proceeds more slowly than the second, that is, the element with the smaller valency has the longer life. In the same disintegration series, elements which emit  $\beta$ -rays have longer lives the greater the atomic mass, whether the valency is odd or even, the odd and even valencies being considered separately. A similar rule holds for elements in the same group of the periodic system, but not in the same pleiad, with certain exceptions. There are very few exceptions to the above statements, and these occur generally in the least well investigated elements. The origin and atomic mass of actinium are discussed, and reasons are advanced for the value 226. The author also discusses the identity of isotopes and analogous radioactive elements, and finally the relationship of the radioactive elements to the periodic classification.

J. F. S.

**Ionisation of Gas during a Chemical Reaction.** ALEXANDRE PINKUS (*Helvetica Chim. Acta*, 1918, **1**, 141—145; *J. Chim. Phys.*, 1918, **16**, 201—227).—With the object of ascertaining whether ionisation occurs during the interaction of two gases, the author has brought the following pairs of gases, (1) nitric oxide and oxygen, and (2) nitric oxide and chlorine, together in a large glass globe under a pressure of 0.25—0.5 atm. The walls of the

vessel were connected by iridioplatinum electrodes with a sensitive electrometer, and the rate of discharge was plotted. In the case of nitric oxide and oxygen, no formation of ions takes place, nor is there any evidence that ionisation occurs during the reaction between chlorine and nitric oxide if the chlorine is not in excess. Should the chlorine be in excess, there is a marked ionisation. The author attributes the ionisation to the intermediate formation of  $\text{NOCl}_2$ . J. F. S.

**Resonance and Ionisation Potentials for Electrons in Sodium Vapour.** JOHN T. TATE and PAUL D. FOOTE (*J. Washington Acad. Sci.*, 1918, 7, 517—525).—In the further investigation of the potentials at which electrons give rise to the emission of rays, experiments have been made on sodium vapour. The resonance potential at which rays corresponding with the *D*-lines are emitted is found to be  $2.12 \pm 0.06$  volts, the value calculated on the basis of Bohr's theory being 2.10 volts. When the potential reaches  $5.13 \pm 0.1$  volts, ionisation of the sodium vapour occurs. This is identical with the value calculated on the basis of Bohr's theory by using the limiting wave-length of the principal series of lines in the sodium spectrum.

The lower potentials found by Wood and Okano (*Phil. Mag.*, 1917, [vi], 34, 177) in their observations on the emission of the *D*-lines by sodium vapour suggest that ionisation of the vapour occurs under the influence of more slowly moving electrons. A full account of this and the previous paper (*A.*, 1918, ii, 94) is to be found in *Phil. Mag.*, 1918, [vi], 36, 64—75. H. M. D.

**Relation of the Electrical Conductivity to the Periodic System of the Elements.** E. GRÜNEISEN (*Ber. Deut. physikal. Ges.*, 1918, 20, 53—62).—According to Benedicks (*Jahrb. Radioaktiv. Elektronik.*, 1916, 13, 351), the atomic conductance, measured by the product of the specific conductance and the atomic volume, is a periodic function of the atomic weight. The conductance data used by Benedicks are not strictly comparable, however, for the influence of temperature is by no means the same for the different elements. It is suggested that conductance data for corresponding temperatures should be used in the comparison of the atomic conductances, and in accordance with the empirical formula referred to in the following abstract, such temperatures are those which bear the same ratio to the characteristic temperatures.

By reference to the data which are available for this comparison, it is shown that the atomic conductance is a periodic function of the atomic weight, and that the value decreases from the first to the eighth group in the periodic table. H. M. D.

**Electrical Conduction of Metals at Low Temperature.** E. GRÜNEISEN (*Ber. Deut. physikal. Ges.*, 1918, 20, 36—52. Compare *A.*, 1913, ii, 377).—By reference to the data for lead,

cadmium, zinc, mercury, gold, platinum, silver, and copper, the author has tested the empirical formula  $w \sim T \cdot F(T/\Theta) \cdot C_p/C_r$  for the influence of temperature on the electrical resistance of metals. In this formula,  $w$  represents the resistance,  $T$  the absolute temperature,  $F(T/\Theta)$  a universal function of  $T/\Theta$ , where  $\Theta$  is the characteristic temperature of the metal according to Debye's theory. It is shown that the formula affords a satisfactory account of the observed variations in the conductivity of metals over a wide range of temperature, and the author infers that the empirical expression affords a close approximation to the statement of the actual law which connects conductivity and temperature.

H. M. D.

**Electronic Theory of the Metals.** TH. WEREIDE (*Ann. Physik*, 1918, [iv], 55, 589—607).—A theoretical paper in which the electronic theory of metals is discussed. It is shown that, apart from a numerical correction, Drude's formula for electric conductivity is unassailable. The formula  $x = \frac{1}{2} \cdot e^2/m \cdot n/v$  has been modified by eliminating the three unknown,  $n$ ,  $l$ , and  $v$ , and in their place introducing the three atomic constants  $\nu$ =vibration number of an atom,  $\epsilon$ =emission number of an atom, and  $a$ =absorption coefficient of an atom. The constant  $a$  bears the relationship  $a = ca$  to Lenard's coefficient  $a$ , where  $c$  is the number of atoms per c.c. The Lenard theory gives then the formula  $x = e^2 \epsilon / 6ca^2 \cdot (e^{h\nu/kT} - 1)h\nu$  for the electric conductivity and a similar formula for thermal conductivity. On the basis of this formula, the reasons for the following points are explained. (1) At high temperatures, the electric resistance is approximately proportional to the absolute temperature. (2) The change in resistance depends on the energy change of the substance. (3) The resistance approaches zero at the absolute zero. (4) The conductivity curve and the atomic volume curves have a similar form. (5) Under similar conditions, the conductivity is greater the greater the electro-affinity of the atoms.

J. F. S.

**Calculation of the Position of the Conductivity Minimum in Neutralisation.**

W. D. TREADWELL (*Helvetica Chim. Acta*, 1918, 1, 97—110).—The author has calculated the position of the conductivity minimum in the neutralisation of (1) a diluted strong acid by a diluted strong base, (2) a weak monobasic acid by a diluted mono-acidic strong base, (3) a mixture of two weak monobasic acids of different strengths by a strong mono-acidic base, and (4) a mixture of a monobasic weak acid and a monobasic strong acid by a strong mono-acidic base. In the first case, the minimum of conductivity lies exactly at the point of neutralisation; in the second case, using equal concentrations of acetic acid and alkali, the minimum occurs when there is an excess of 0.4% of acid present, or generally if  $x$  represents the number of c.c. of alkali of concentration  $c_2$  which is present to 1 c.c. of acid of concentration  $c_1$ , then  $x = c_1/c_2 \times k_1/k_2 + \sqrt{k_1} \cdot l_{OH}/l_H$ . The influence of decreasing

strength and concentration of the acid on the position of the minimum is also calculated. The conductivity minimum is calculated in the case of a number of acids, and these values are compared with the experimental values of Thiel and Roemer. Good agreement is found between the two sets of values. J. F. S.

**Calculation of the Electrochemical Normal Potential:**

KARL F. HERZFELD (*Ann. Physik*, 1918, [iv], 56, 133—160).—A mathematical paper in which the normal potential of the ions is calculated on the assumption that the entropy constant of the dissolved ions is the same as that of the corresponding atoms. The numerical results of this calculation differ from the experimental values, but the amount of divergence is the same for ions of equal mobility. The divergences are therefore attributed to complex formation of the ions with water. From these calculations, formulæ for the solubility of salts are deduced. In open cells, only the positive ions are in equilibrium, for the electrons only slowly reach equilibrium; hence the cell at first only approximates to a reversible element. In this connexion, the mechanism of the semi-permeable membrane is discussed. Calculations are made for metals of the single potential, the contact potential, and the electron number. The Helmholtz equation is not strictly applicable to single electrodes. J. F. S.

**[Potentials due to the Flow of Electrolytes through Capillary Tubes and the Stability of Colloids.]**

H. R. KNUYT (*Kolloid Zeitsch.*, 1918, 22, 81—98).—The potential differences produced by the flow of solutions of electrolytes through a capillary tube have been measured in experiments with solutions of different chlorides. In the apparatus used, the capillary tube formed part of the connexion between two glass vessels fitted with silver electrodes coated with silver chloride, and the chloride solution was made to pass through the glass capillary from one vessel to the other under the influence of a constant pressure difference.

The results obtained with solutions of potassium, barium, and aluminium chloride show that the influence of the cation on the potential difference between the electrodes depends very largely on the valency of the cation. The relations are in general very similar to those which were found by Powis (A., 1915, ii, 137) in the investigation of the influence of the three chlorides on the cataphoresis of hydrocarbon oil emulsions. In both series of observations, the effects are attributable to the adsorption of electrolytes. The author's experiments seem to show, however, that in very dilute solutions the contact potential is increased by the presence of the electrolyte. It is probable that this fact explains the well-known peptonising action of electrolytes in very dilute solution and the essential importance of small quantities of electrolytes in connexion with the stability of colloidal systems.

H. M. D.



**Passivity of Chromium. II.** A. H. W. ATEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 1119—1134. Compare this vol., ii, 183).—In the further investigation of the electrochemical behaviour of chromium, measurements have been made of the potential of chromium when subjected to anodic and cathodic polarisation.

The phenomena associated with the anodic polarisation of electrolytic chromium depend to some extent on the nature of the metal on which the chromium has been deposited. If the metal immersed in a solution of chromous sulphate is anodically polarised with a sufficiently strong current, the chromium becomes passive, but when the current is interrupted, the potential of the metal is found to be more negative than before polarisation. The passivation during anodic polarisation and activation after this treatment are shown by chromium which has been deposited on copper, silver, or gold. The degree of activation after anodic polarisation increases with the strength of the polarising current.

Chromium, prepared by Goldschmidt's process, which has been activated by treatment with molten zinc chloride, or a mixture of sodium and potassium chlorides, may be anodically polarised in a solution of potassium chloride without becoming passive. The resistance offered by the metal to the action of the polarising current is greater when the strength of the current is gradually increased than when the current strength is increased rapidly. The resisting power of the metal is smaller when the chromium has been previously subjected to cathodic polarisation. If the chromium has been rendered passive by anodic polarisation in a solution of potassium chloride, the active condition may be restored by heating the solution. This change occurs even when the polarising current is continued during the heating of the solution, and, on cooling, the chromium remains in the active condition provided that the current is not too strong.

H. M. D.

**Allotropy of Cadmium. VI.** ERNST COHEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 1177—1185).—A criticism of the conclusions drawn by Getman from his observations (compare A., 1917, ii, 533) on the *E.M.F.* of  $\text{Cd}|\text{CdSO}_4|\text{Cd}$  amalgam cells. According to Getman, the influence of temperature on the *E.M.F.* of cells containing 8% cadmium amalgam points to the existence of two allotropic forms of cadmium with a transition point at 37.5°. The discontinuity in the temperature coefficient of the *E.M.F.* at this temperature is, however, to be attributed to a change in the amalgam at this temperature. According to Bijl's investigations (A., 1903, ii, 6), the 8% amalgam used by Getman undergoes transformation at about 40°, and the resulting change in the electromotive behaviour of the amalgam has been erroneously attributed by Getman to the transformation  $\text{Cd-}\alpha$  into  $\text{Cd-}\beta$ . The actual results obtained by Getman are considered to afford confirmation of the views which have been previously put forward

by the author as a result of his investigation of the allotropy of cadmium (A., 1914, ii, 52, 652; 1915, ii, 40, 144). H. M. D.

**Magnetic Susceptibility and Electric Resistivity.** F. H. LORING (*Chem. News*, 1918, 117, 229—231).—A theoretical discussion of magnetic susceptibility in which the author assumes that ferro-, para-, and dia-magnetic qualities are to be explained in terms of atomic and molecular currents which are dependent on the specific resistances of the elements concerned. H. M. D.

**The Influence of the Finite Volume of Molecules on the Equation of State.** MEGH NAD SHAHA and SATYENDRA NATH BASU (*Phil. Mag.*, 1918, [vi], 36, 199—202).—Starting from Boltzmann's entropy principle, the authors have obtained a new equation of state which may be written in the form  $pV = N K \theta r / 1 - e^{-x}$ , where  $x = \beta p / K \theta$ . In these equations,  $K$  represents Boltzmann's gas constant,  $N$  the number of molecules contained in volume  $V$ ,  $\theta$  the temperature, and  $\beta = 8 \times$  volume of a single molecule. From this equation of state, the critical volume  $V_c = 3.166b$  and  $K = 3.513$ . The values of  $V_c$  derived from the van der Waals and Dieterici equations are  $3b$  and  $2b$  respectively, and the values of  $K$  2.66 and 3.695 respectively. H. M. D.

**The Course of the Values of  $a$  and  $b$  for Hydrogen at different Temperatures and Volumes. II.** J. J. VAN LAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, 20, 1195—1212. Compare this vol., ii, 185).—A theoretical paper in which the pressure-volume relations are further discussed in reference to the variability of  $a$  and  $b$ . H. M. D.

**Isothermals of Monatomic Substances and their Binary Mixtures. XIX. Vapour Pressures of Neon between the Boiling Point and the Critical Point.** P. G. CATH and H. SAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, 20, 1160—1162).—The vapour pressures of liquid neon have been measured at temperatures ranging from  $24.42^\circ$  to  $44.43^\circ$  (abs.). The results are satisfactorily reproduced by the formula  $\log p = -65.061 + 2.8191T + 0.01118T^2$ , where  $p$  denotes the vapour pressure in atmospheres.

A comparison of the reduced vapour pressure curves for oxygen, nitrogen, argon, neon, and hydrogen has been made, and from this it appears that the divergence between hydrogen and neon is much greater than that between neon and argon, in spite of the fact that the critical temperature of neon is relatively low.

H. M. D.

**The Characteristic Equation of Fluids.** PIERRE WEISS (*Compt. rend.*, 1918, 167, 232—235. Compare *ibid.*, 1918, 167, 3).—The isochores for air, ethylene, ether, and isopentane are

15°—2

given, and in each case they consist of rays of straight lines each showing one point of inflection. They resemble the magnetic isotherms (*loc. cit.*). W. G.

**The Entropy of a Metal.** H. STANLEY ALLEN (*Proc. Physical Soc. London*, 1918, **30**, 215—220).—The formula derived by Ratnowsky (*Ber. Deut. physikal. Ges.*, 1914, **16**, 1033) for the entropy of a substance in the solid state is found to give values for a number of metals in very close agreement with those recorded by Lewis and Gibson (this vol., ii, 29). The assumptions made by Ratnowsky in deducing his entropy formula are examined, and the conclusion is drawn that these are justified as being at least approximately true. H. M. D.

**Boundaries of Existence of the Liquid State.** JULIUS MEYER (*Zeitsch. Elektrochem.*, 1918, **24**, 138—139. Compare Herz, this vol., ii, 150).—A criticism of Herz's definition of the boundaries of the liquid state. Herz makes the melting point and the critical point the limits of existence of a liquid, whereas Meyer is of opinion that no such points can be specified. J. F. S.

**Boundaries of Existence of the Liquid State.** W. HERZ (*Zeitsch. Elektrochem.*, 1918, **24**, 139. Compare preceding abstract).—Polemical; an answer to Meyer (*loc. cit.*). J. F. S.

**Boiling Points of the Paraffins.** GERVAISE LE BAS (*Chem. News*, 1918, **117**, 241—242).—A theoretical paper in which it is shown that the rule of Hinrichs and Naumann, which states that the more the chain of a molecule is branched the lower will be the boiling point, is not generally to be followed. It is shown that the boiling point depends on whether the hydrogen attached to the  $\beta$ -,  $\gamma$ -,  $\delta$ -, etc., carbon atoms has been displaced by methyl groups. In dealing with this question, it is necessary to consider the formulae of *iso*-compounds. It is the practice of writing the formula of an *iso*-compound thus,  $\begin{smallmatrix} \text{Me} \\ \text{Me} \end{smallmatrix} > \text{CHR}$ , which tacitly assumes that it consists of two similar methyl groups attached to one carbon atom. From the point of view of the boiling points, this is not true. This class of structure involves the displacement of an hydrogen atom attached to the  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -, etc., carbon atom of the hydrocarbon by a single methyl group. The difference in boiling point due to this structure is  $6^\circ$  or  $7^\circ$  when substitution of a  $\beta$ -methylene group has been effected, and slightly more,  $9^\circ$ , when the  $\gamma$ -methylene group has been substituted. J. F. S.

**Method for the Determination of the Relation between Vapour Pressures and their Corresponding Temperatures at Pressures of less than Five Millimetres.** W. R. HAM, J. C. CHURCHILL, and H. M. RYDER (*J. Franklin Inst.*, 1918, **186**, 15—28).—The substance under investigation is subjected to slow distillation and condensation in a closed system of considerable

capacity, the pressure in which is reduced to a low value determined with the aid of a McLeod gauge which is attached to the closed system. The system is also connected with a reservoir of pure dry hydrogen, the object of this arrangement being to ensure accuracy in the readings of the McLeod gauge. The pressure in the apparatus is varied by running the pump at different speeds, the driving motor being suitably controlled. The liquid in the distilling flask is electrically heated by passing a current through a platinum wire immersed in the liquid, and the vapour evolved passes through a side-tube, in which a thermometer is supported, to a condenser, from which the condensate drops into a receiver. For a given rate of working of the pump, a series of observations is made in which the liquid is distilled at different rates determined by the number of drops of liquid which fall from the end of the condenser tap into the receiver in a fixed interval of time. In each of these experiments, the temperature of the vapour registered by the thermometer is recorded. By plotting the temperature against the rate of distillation, a smooth curve is obtained, and by extrapolation to zero rate of distillation, a temperature is obtained which corresponds with the pressure in the closed system as measured by the McLeod gauge.

Results obtained for acetophenone by this method show close agreement with the values obtained for this substance by Kahlbaum, who measured the depression of a barometric column. The results may be expressed by the equation  $\log P = 19.696 - 72.540 \times 0.993944^T$ , or by the equation  $\log P = 16.152 - 3390.96/T - 534192.38/T^2$ .

H. M. D.

**The Solutions of Gases in Liquids.** FÉLIX MICHAUD (*Ann. Physique*, 1918, [ix], 9, 203—232, 233—258. Compare A., 1917, ii, 122).—A theoretical discussion of the subject. Contrary to Duhem's conclusions, the presence of a gas in solution at constant temperature does not always lower the vapour pressure of the solvent. That only occurs if the pressure of the solution is maintained constant by means of an auxiliary, insoluble gas. It is possible to obtain a simple formula from which the vapour pressure of the solvent can be calculated in terms of the pressure of the gas, the formula being really an expression of Raoult's law for a very soluble, normal gas which obeys Henry's law. A cryometric study of solutions of gases leads to similar results.

From a study of the calorific phenomena which accompany the solution of a gas, a simple expression for the entropy of reversible solution can be obtained. A formula is also established connecting the specific heat of a solution of a gas in a liquid with the coefficient of solubility of the gas.

W. G.

**Iso-piestic Solutions.** W. R. BOUSFIELD (*Trans. Faraday Soc.*, 1918, 13, 401—410).—Solutions of various salts were placed in an exhausted desiccator and allowed to remain at constant temperature until the several solutions were in equilibrium with

one another. The resulting solutions have the same vapour pressure at the temperature of the experiments, and are termed iso-piestic.

Results obtained at 18° show that iso-piestic solutions of potassium chloride, sodium chloride, and lithium chloride contain different numbers of molecules of water per molecule of salt. The value of this molecular ratio ( $h$ ) for a saturated solution of potassium chloride is 12.41, whilst for the iso-piestic solutions of sodium chloride and lithium chloride  $h=14.16$  and 17.07 respectively. Although the total quantities of water thus differ appreciably for the three salts, it is calculated that the quantities of uncombined water are very nearly the same. The differences in  $h$  are due to differences in the quantities of combined water, for which the respective molecular ratios are approximately 1, 3, and 6.

Observations in which the dry salts were exposed to the action of water vapour at different pressures lead the author to the conclusion that for substances which do not form crystalline hydrates there is, at a given temperature, a certain pressure of aqueous vapour below which the dry substance will not take up water vapour, and if the substance is not dry originally, it will become so provided the pressure of aqueous vapour is lower than this critical value, which is called the critical hydration pressure of the substance.

H. M. D.

**Measurement of Very Low Temperatures. XXVII. Vapour Pressures of Hydrogen in the Neighbourhood of the Boiling Point and between the Boiling Point and the Critical Temperature.**

P. G. CATH and H. KAMERLINGH OMNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 1155—1159).—The vapour pressures of liquid hydrogen have been determined at temperatures between 24.59° and 32.93° (abs.). The results obtained are satisfactorily represented by the formula  $T \log p = -56.605 + 3.8015T - 0.10458T^2 + 0.003321T^3 - 0.00005102T^4$ , in which  $p$  represents the pressure in international atmospheres. Further measurements of the vapour pressure in the neighbourhood of the boiling point have given for this 20.39° (abs.). This value is 0.04° lower than the value obtained in a previous series of measurements.

H. M. D.

**The Saturated Vapour Pressures of Octa-atomic Substances.** E. ARIÈS (*Compt. rend.*, 1918, **167**, 118—122).—The formula derived for the saturated vapour pressures of octa-atomic compounds is  $\Pi = \tau^{29/10} Z/x$ , where

$$x = [1 + (1 - \tau)(0.88 - \tau) / \{0.8 + (1 - \tau)^2\}] \tau^{19/10}.$$

The values, observed and calculated, are in fairly close agreement in the cases of methyl formate, ethyl bromide, and ethyl chloride, but in the cases of acetic acid and ethane it is not possible to obtain satisfactory verifications.

W. G.

**Ebullioscopic Determinations with a Common Thermometer.** C. C. KIPLINGER (*J. Amer. Chem. Soc.*, 1918, **40**, 1020—1023).—An arrangement is described whereby an ordinary

thermometer having a solid stem graduated in degrees may be read to hundredths of a degree with an error not exceeding 1%. A meter rod graduated in mm. is attached to a stand and equipped with a sliding peep-sight made from a strip of thin sheet metal. This rod is set parallel with the thermometer, the hole of the peep-sight being at a distance of 6 inches from the thermometer scale. The thermometer is fitted with a pen-shaped metallic indicator tapered to a width at the point equal to the apparent width of the capillary. The indicator is blackened, bent so that the tip is at a distance of 3 mm. from the scale, and attached to the thermometer by a screw clamp. The position of the mercury meniscus with reference to the nearest scale division is determined as follows. For clearness of explanation, let the meniscus be denoted by the letter  $P$ , the nearest scale division by  $D$ , and the tip of the indicator by  $A$ . Light is projected by a mirror on to the meniscus. The sliding peep-sight is moved until the scale division  $D$  is just hidden behind the tip  $A$  of the indicator; if the position of the peep-sight on the rod is denoted by  $X$ , then  $XAD$  is a straight line. The peep-sight is then moved to a position  $Y$  in which the gleam of the meniscus  $P$  is just hidden behind the tip  $A$ . The position of the meniscus  $P$  with reference to  $D$  is thus determined by the angle  $XAY$ ; the distance  $XY$  once known, the apparatus may be dismantled, set up again, and the position of  $P$  with reference to  $D$  as definitely fixed as before, provided the indicator has not been moved relatively to the scale mark  $D$ .

In using the apparatus to determine molecular weights ebullioscopically, the principle adopted is to vary the concentration of the solute under examination until the rise of the b. p. is exactly the same as that produced by a substance of known molecular weight. For example, about 30 grams of carbon tetrachloride (constant 48) are placed in the weighed boiling tube with a known amount of borneol. When the temperature has become constant, the angle  $XAY$ , expressed in terms of divisions of the mm. scale, is determined as above, thus establishing the point  $P$ . The barometer is read, and the tube and its contents are weighed to determine the true weight of the solvent. Knowing the weight of the solvent and of the solute, and the molecular weight of the latter, the rise of the b. p. is calculated. The apparatus is cleaned and weighed, and a weighed amount of the substance of unknown molecular weight is added, together with a few grams of solvent. The solution is brought to the b. p., and small portions of solvent are added from time to time until the meniscus reaches the same point as in the borneol trial, as determined by the angle  $XAY$ . If too much solvent has been added, the condenser may be detached to allow some of the solvent to evaporate. When the adjustment is correct, the tube and its contents are weighed to ascertain the weight of the solvent. The rise of the b. p. is known from the borneol trial, hence the molecular weight can be calculated. In both cases, the same point  $D$  on the thermometer has been used

for reference, hence a calibrated thermometer is unnecessary. The height of the flame must be kept constant throughout the work.

Molecular weights (the average of a series of determinations) determined in this manner compare favourably with those obtained by the usual method. C. S.

**A Laboratory Apparatus for Distilling in [Superheated] Steam under Reduced Pressure.** C. HARRIES and REINOLD HAARMANN (*Ber.*, 1918, 51, 788—790).—Steam at 3—4 atmos. pressure is admitted through a throttle-valve into a superheating chamber maintained at about 300°, and then into the substance in the exhausted distilling flask, the neck of which is filled, by a simple device, with small pieces of glass rod in order to break up froth and prevent spirting. The apparatus is completely described with illustrations, and it is claimed that substances otherwise very non-volatile can be purified easily by distillation in this way, and hygroscopic salts deprived of solvent water. J. C. W.

**Definitions of Explosive Substance, Explosive Action, and Thermite.** HANS SCHIMANK (*Zeitsch. Elektrochem.*, 1918, 24, 213—214).—An explosive substance is defined as a substance which undergoes a very rapid exothermic change with the formation of gaseous products. Explosive action is differentiated from such actions as occur in overheated steam boilers. Thermite is a system which is capable of undergoing rapid exothermic reaction without the formation of gaseous products. J. F. S.

**Connexion between the Atomic Weights, Densities, and Heats of Reaction of the Elements.** KARL FEHRLE (*Physikal. Zeitsch.*, 1918, 19, 281—286).—A theoretical paper in which the author derives an expression for the heat of formation of a compound which involves only the atomic weights of the reacting elements and the densities of the elements and the compound formed. H. M. D.

**Thermal Properties of Sulphuric Acid and Oleum.** ALFRED W. PORTER (*Trans. Faraday Soc.*, 1918, 13, 373—399).—The thermal data bearing on the concentration of sulphuric acid by evaporation have not hitherto been determined by experiment, and in view of the technical importance of the quantities in question, the author has attempted to supply the requisite information by indirect methods involving thermodynamical relations. The thermal data for the ordinary temperature are utilised in conjunction with calculations which give the variation of the heats of solution and dilution with temperature, and from these results the heats of total evaporation of water from sulphuric acid solutions at different temperatures are derived. A method of graphical representation, which facilitates the determination of the thermal data which may be required in a particular case, is described.

In the second part of the paper, similar methods are employed

in the calculation of the thermal data for oleum (fuming sulphuric acid), and in particular of the heats of total evaporation or condensation of sulphur trioxide vapour for sulphuric acids containing 80–90% of sulphur trioxide. H. M. D.

**Experimental Determination of the Fictitious Heat of Solution.** ERNST COHEN and H. R. BRUINS (*Zeitsch. physikal. Chem.*, 1918, **93**, 43–58).—By the term fictitious heat of solution is to be understood the heat change which occurs when 1 gram-molecule of a substance at a measured temperature and pressure dissolves in an unlimited amount of its own saturated solution at the same temperature and pressure. Four methods of determining this value are described, and of these two have been used to determine the value for cadmium iodide in water. To measure the fictitious heat of solution of a salt  $KA$ , two galvanic elements,  $XY$ , are connected so as to oppose one another, and the resulting  $E.M.F.$  is measured.

X.			Y.		
Electrode reversible with respect to K.	Saturated solution of $KA$ without solid phase.	Electrode reversible with respect to A.	Electrode reversible with respect to A.	Very dilute solution of $KA$ .	Electrode reversible with respect to K.

According to the Gibbs-Helmholtz equation,  $E_c = n\epsilon(E_c - T \cdot dE/dT)0.2389$  gram cal., where  $E_c$  is the  $E.M.F.$  and  $E_c$  the chemical energy of the double cell; also  $E_c = W - F$ , where  $F$  is the fictitious heat of solution and  $W$  the heat of solution of the dilute solution of  $KA$ . Consequently,  $F = W - n\epsilon(E_c - T \cdot dE/dT)$  gives the value of  $F$ .

In the second method, the combination

Electrode reversible with respect to K.	Saturated solution of $KA$ without solid phase.	Dilute solution of $KA$ .	Electrode reversible with respect to K.
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is measured, and from the equation  $F = W - n/n_1 \cdot \epsilon(E_c - T \cdot dE/dT)0.2389$  gram cal., the heat of solution is obtained; the symbols have the same meaning as before;  $n_1$  is the number of gram ions transported from the saturated solution to the dilute solution by the passage of  $\epsilon = 96,494$  coulombs. This method is complicated by the contact potential existing at the boundary of the two solutions.

The third method consists in measuring the  $E.M.F.$  and temperature coefficient of the cell  $X$  and of the same cell with solid phase  $Y$ , and then using the equation of the same kind as those given above, the value of  $F$  follows. A series of  $E.M.F.$  determinations of these cells has been made at  $16^\circ$ ,  $18^\circ$ ,  $20^\circ$ ,  $22^\circ$ , and  $24^\circ$ , and the temperature coefficient calculated for the case of cadmium iodide and the value  $-1246$  gram cal. determined at  $18^\circ$ .

The fourth method depends on the measurements made in the last method; the relationship

$$(dE/dT)_T = (dE/dT)_{X1} + (dE/dC)_T \cdot (dC/dT)$$



exists between the temperature coefficients of  $X$  and  $X_1$ ;  $dC/dT$  is the temperature coefficient of the solubility, by substitution  $F = [T \cdot (dE/dC)_T \cdot (dC/dT)]/46,105$  gram cal. Hence to determine  $F$ , the values of  $(dE/dC)_T$  and  $(dC/dT)$  have to be determined.

These measurements have been made for cadmium iodide; the solubility of cadmium iodide is expressed by the equation  $C = 44.18 + 0.0828t + 0.000183t^2$ , consequently  $(dC/dT)_{18} = +0.08939$ . To ascertain the value of  $dE/dC$ , the *E.M.F.* of a number of elements  $\text{Cd}/\text{CdI}_2$  of different concentrations have been measured at  $18^\circ$ , whence the dependence of the *E.M.F.* on concentration is given by the equation  $E_{18} = 0.43150 + 0.000283C - 0.00001428C^2$ , so that  $(dE/dC)_{18} = -0.001023$  volt per cent. Using these values,  $F = -1227$  gram cal. at  $18^\circ$ . J. F. S.

**Relative Volume Change which occurs on Mixing two Chemically Indifferent Gases, and its Measurement by Refraction of Light.** PAUL FUCHS (*Zeitsch. physikal. Chem.*, 1819, 92, 641—676).—The change in total volume on mixing two chemically indifferent gases has been determined over the whole range of mixtures for the pairs nitrous oxide–nitrogen, carbon dioxide–nitrogen, oxygen–nitrogen, nitrous oxide–carbon dioxide, nitrous oxide–oxygen, oxygen–carbon dioxide by means of refraction measurements. The Haber-Löwe interferometer was used for this purpose, and the measurements were made at ordinary temperature and pressure. In every case, there is an increase in volume on mixing which is greater the more the two components differ in their physical behaviour. The volume change does not correspond with the ratio in which the gases are mixed, but reaches a maximum at a point beyond the equal concentration point in the sense that the maximum change lies with mixtures containing more than 50% of the gas of smaller critical temperature. The maximum volume change lies nearer to the 1:1 mixture the more the components resemble one another. The van der Waals's expression,  $\Delta v = x(1-x)[\{a_1+a_2-2a_1a_2\}/MRT - \{b_1+b_2-2b_1b_2\}]$ , was tested by means of the data obtained and found to be qualitatively in accord with the general results, but not strictly quantitatively correct. The dispersion of the gaseous mixtures is markedly different from that of the sum of the two components. J. F. S.

**The Vapour Pressure of Dissociating Substances and the Volatilisation of Ammonia.** RUD. WEGSCHEIDER (*Zeitsch. anorg. Chem.* 1918, 103, 207—220).—An expression has been evolved for calculating the vapour pressure curves of dissociating substances, particularly those which on volatilisation dissociate partly into two molecules. The data required for the calculation are: the specific heats of solid (or liquid) and of dissociated and undissociated vapour; the heat of evaporation without dissociation and the heat of dissociation for each temperature; the dis-

sociation constant and the vapour pressure for one temperature. The expression is used to examine the probability of different explanations put forward to account for the two vapour pressure curves of ammonium chloride. This substance is dimorphous, with a transition point at  $184.5^{\circ}$ , but the dimorphism will not account for the form of the curves unless the heat of transformation is at least  $-3000$  cal., whereas the observed value is only  $-1030$  cal. The assumption of further polymorphism with a second transition point either above or below  $184.5^{\circ}$  is shown to be invalid. The possibility is not excluded, however, that the ordinary form of ammonium chloride is labile, changing into the stable form only at high temperatures in presence of moisture. When perfectly dry, this labile form volatilises without dissociation, and its vapour pressure must be greater than the partial pressure of the undissociated molecules in the vapour of the stable form. An alternative explanation of the contradictory results sometimes obtained is that, whilst the ordinary form of ammonium chloride is stable, at times a labile form is obtained which when dry volatilises unchanged.

E. H. R.

**The Principles of Diffusion, their Analogies and Applications.** HORACE T. BROWN (T., 1918, 113, 559—585).—A lecture delivered before the Chemical Society on June 6th, 1918.

D. F. T.

**Condition of Double Salts in Aqueous Solution.** D. MERRILL TORRANCE and NICHOLAS KNIGHT (*Chem. News*, 1918, 117, 270—272. Compare Maxwell, A., 1917, ii, 562).—The changes occurring in the diffusion of solutions prepared from sodium aluminium sulphate, copper potassium sulphate, copper ammonium sulphate, magnesium ammonium sulphate, and potassium chromium sulphate have been examined at different temperatures and at different concentrations. The results indicate that the double salts are largely dissociated into the respective simple salts. The relative rates of diffusion appear to be influenced appreciably by ionic hydration.

H. M. D.

**Hydrogen Ion and Hydrogen Bound to Ionogens: Chemistry of Electrolytic Dissociation.** A. HANTZSCH (*Zeitsch. Elektrochem.*, 1918, 24, 201—213).—A theoretical paper in which the intramolecular change involved in the formation of pseudo-acids is discussed. In this connexion, the position and method of linking of the hydrogen atom are considered, and theories put forward to explain the behaviour of the hydrogen in the different positions. The author proposes to substitute for the optical method of determining constitution the action of the substance in question on diazo-esters. The pseudo-acid is without action on the diazo-ester, whereas the true acid liberates nitrogen freely. A modification of the processes generally held to be occurring in ionisation is discussed.

J. F. S.

**Liquid Crystals.** TARINI CHARAN CHAUDHARI (*Chem. News*, 1918, 117, 269—270).—For closely related compounds, the intervals of temperature over which the liquid crystalline phase is stable appear to be simply related. Smits's dynamic theory of polymorphism in its application to liquid crystalline forms is considered to be unsatisfactory. There appears to be no definite connexion between the constitution of compounds and their capacity to form liquid crystals, and the author advances the view that the formation of such crystals is a general property of organic substances which melt without decomposition. H. M. D.

**Non-molecular Structure of Solids.** ARTHUR H. COMPTON (*J. Franklin Inst.*, 1918, 185, 745—774).—The fact that the X-ray examination of certain simple crystals has shown that these have a non-molecular structure, suggests that this may be characteristic of all solid substances. In support of this hypothesis, a number of arguments are put forward, and the conclusion is drawn that in the solid state of aggregation the atoms are so intimately intermingled that particular molecules cannot be said to have any real existence.

The dependence of crystal form on chemical composition, X-ray observations, and considerations relative to the law of Dulong and Petit and the nature of cohesion, all suggest that the atoms of a crystalline solid oscillate about a mean position of stable equilibrium, and a comparison of the nature of cohesive forces with those which are concerned in chemical combination indicates that these are of the same nature and of the same order of magnitude. In this connexion, it is pointed out that there is a close parallelism between the melting temperatures and the "atomic heats of formation" for a large number of different substances. The melting point may be supposed to afford an approximate measure of the firmness with which the molecules are held together in the solid substance, whilst the "atomic heat of formation," obtained by dividing the molecular heat of formation by the number of atoms in the molecule, may be supposed to measure the intensity of the intramolecular forces.

Although certain properties of solid matter have been explained on the assumption that the ultimate atoms are definitely grouped into molecules, the author shows that recent work tends to replace the older methods of explanation by others in which no such assumption of molecular structure is specifically involved.

H. M. D.

**Connexion between Colour and Degree of Dispersity.** F. KIRCHHOFF (*Kolloid Zeitsch.*, 1918, 22, 98—102).—The view that the colour of disperse systems is determined by the size of the colloidal particles is considered in reference to the colours of the alkali metal sols and the changes which accompany the alteration in the valency of metal ions and the formation of complex ions. The relations exhibited suggest that the colour is fundamentally

connected with the size of the disperse particles, whether these are atomic, ionic, or colloidal in nature. H. M. D.

[**Time Reactions in Colloidal Systems.**] D. VORLÄNDER (*Kolloid Zeitsch.*, 1918, **22**, 103—104).—According to Reitsstötter (this vol., ii, 102), a solution of potassium ferrocyanide which has been used to bring about the coagulation of colloidal aluminium hydroxide gives no blue colour on the addition of a very dilute solution of a ferric salt. In the author's opinion, the apparent absence of a reaction is to be attributed to the fact that the reaction between ferrocyanide and ferric salt is a relatively slow one, the slow rate being determined by the colloidal nature of the ferric salt solution. Salts, acids, and other substances have a considerable influence on the speed of the reaction.

The reaction between ferricyanide and ferrous salt, on the other hand, takes place instantaneously, and in this system no colloidal particles are involved. A similar difference between the speeds of corresponding reactions is found in the action of hydrogen sulphide on stannic and stannous salts. In the case of the stannous salts, the ionic reactants give rise to an immediate precipitation of the metal sulphide. H. M. D.

**Rhythmic Diffusion Structures in Gelatin-Salt Jellies.** II. W. MOELLER (*Kolloid Zeitsch.*, 1918, **22**, 155—163. Compare A., 1917, ii, 410).—If drops of hydrochloric acid are allowed to fall on to a semi-liquid gelatin jelly containing sodium chloride, the semi-liquid condition being produced by suitably adjusting the temperature to which the previously cooled jelly is raised, diffusion of the acid takes place with the formation of well-developed spherites which resemble closely the spheritic structures that are found in plant cells. The formation of these spherites in the diffusion of the acid through the salt-jelly is interpreted in terms of the theory of jelly structure which has been put forward in previous papers. H. M. D.

**Coagulation of Roughly Dispersed Gold Hydrosols.** ARNE WESTGREN and J. REITSSTÖTTER (*Zeitsch. physikal. Chem.*, 1918, **92**, 750—762).—The velocity of coagulation of gold hydrosols with large diameters has been determined in the following manner. To a quantity of the sol sufficient sodium chloride solution was added to produce rapid coagulation; after measured intervals of time, 10 c.c. of the mixture were withdrawn and stabilised by the addition of gelatin, and the number of non-coagulated particles was counted. Seven series of measurements were carried out, and from the results it is shown that the theory of Smoluchowski (A., 1917, ii, 297) on the process of coagulation is fully confirmed. The radius of attraction of the particles is slightly more than twice the radius of the particles themselves, which indicates that the particles must almost touch before they unite. J. F. S.

**Equilibrium of the Ternary System: Water, Sodium Sulphate, and Ammonium Sulphate.** CAMILLE MATIGNON and FERNAND MEYER (*Ann. Chim.*, 1918, [ix], 9, 251—292).—A full account of work already published (compare this vol., ii, 66, 67).

W. G.

**Velocity of the Reaction between Nitric Oxide and Oxygen.**

M. BODENSTEIN (*Zeitsch. Elektrochem.*, 1918, 24, 183—201\*).—With the object of settling the controversy between Lunge and Berl and Raschig on the oxidation of nitric oxide in the lead chamber, the author has determined the velocity of oxidation of nitric oxide by oxygen. The two gases were mixed at temperatures from 0° to 90° and at low pressures, and the rate of change was followed by the decrease of pressure. The reaction proceeds strictly according to the equation for reactions of the third order,  $dx/dt = kC_{O_2}C_{NO}^2$ , and the velocity falls considerably with increase in temperature. The velocity is not affected by the addition of nitrogen peroxide, sulphur dioxide, or water vapour. From this it is argued that the oxidation of sulphur dioxide is not catalysed by oxides of nitrogen. The experimental results of Lunge and Berl, suitably recalculated, agree very well with the present work, and those of Raschig agree fairly well beyond the point where 50% of change has occurred. The experimental methods employed by Lunge and Raschig are discussed in the light of the present knowledge of the solubilities of the higher oxides of nitrogen. From this discussion, it is shown that nitric oxide and nitrogen peroxide exist in a constant equilibrium with nitrogen trioxide, which is destroyed with great rapidity in the presence of alkali hydroxide or concentrated sulphuric acid. It is shown that only those results dealing with changes above 50%, obtained by the methods of Raschig and Lunge, are trustworthy and usable. Consequently, the view of Raschig, that nitric oxide is rapidly oxidised to the trioxide, which is then slowly oxidised to the peroxide, is no longer tenable.

J. F. S.

**Velocity of Oxidation of Nitric Oxide.** E. BRINER and E. FRIDÖRI (*Helvetica Chim. Acta*, 1918, 1, 181—185).—The kinetics of the oxidation of nitric oxide have been studied. Mixtures of oxygen and nitric oxide in proportions in which they occur in the production of nitric acid from the atmosphere have been allowed to pass along a series of tubes at constant temperature, and fitted with a series of taps whereby the gases could be removed at various points. The gaseous product was divided into two portions, one condensable by an alcohol-carbon dioxide refrigerant and the other by liquid air. It is shown that if the concentration of the oxygen is regarded as constant, the reaction is of the second order, but if the oxygen concentration is considered, the reaction corresponds with one of the third order and follows the equation  $dx/dt = kC_{O_2}C_{NO}^2$ . With regard to the influence of temperature

\* and *Zeitsch. angew. Chem.*, 1918, 31, I, 145—148.

on the reaction, it is shown that over the interval  $0^{\circ}$  to  $60^{\circ}$ , lowering the temperature  $10^{\circ}$  increases the velocity 10–20%.

J. F. S.

**The Saponification of Fats.** J. P. TREUB (*J. Chim. phys.*, 1918, 16, 107–174).—A résumé of work already published (compare A., 1917, ii, 528; this vol., ii, 71).

W. G.

**Influence of Foreign Substances on the Activity of Catalysts. IV. Experiments with Palladium Hydrosol in the Presence of Mercury and Mercuric Oxide.** C. PAAL and WILHELM HARTMANN (*Ber.*, 1918, 51, 711–737).—In the course of many experiments on the catalysis of mixtures of hydrogen and oxygen by colloidal palladium or platinum, it has been observed that the catalyst becomes more or less passive in time if the gases are kept over mercury, and that, in all cases, if the catalyst remains in contact with mercury, it soon becomes quite inactive, even for the hydrogenation of nitro-compounds and unsaturated substances. Consequently, the authors have made an exhaustive study of the influence of ordinary and colloidal mercury and mercuric oxide on the catalysis of hydrogen and oxygen, and a few experiments on hydrogenations by palladium hydrosol.

The results show that palladium hydrosol has a remarkable power of converting mercury and mercuric oxide into colloidal solution, the oxide much more readily, whereby the palladium permanently loses its power of activating hydrogen, and thus catalysing processes of reduction, but does not suffer as a catalyst of hydrogen peroxide. It may be that a palladium-amalgam hydrosol is formed.

The sodium protalbinat used as a protection to the palladium hydrosol has no influence of itself on mercury. It is the colloidal palladium which causes these to enter the colloidal state. This protective colloid does, however, "peptisate" mercuric oxide in an atmosphere of hydrogen.

J. C. W.

**Atomic Structure and Röntgen Spectra. I.** A. SOMMERFELD (*Physikal. Zeitsch.*, 1918, 19, 297–307).—A theoretical paper in which the arrangement of the rings of electrons in the atoms is discussed on a mathematical basis.

H. M. D.

**The First and Second Electron Rings of the Atoms.** JAN KROO (*Physikal. Zeitsch.*, 1918, 19, 307–311).—On the assumption that the high-frequency lines in the  $K_{\alpha}$  series are due to the displacement of a single electron between rings which correspond respectively with one and two quanta, it is shown that experimental observations are consistent with the view that the former contains three electrons and the latter eight.

H. M. D.

**The Atomic Theory. X. Space-filling Numbers and the Scale of Corresponding States.** RICHARD LORENZ (*Zeitsch. anorg. Chem.*, 1918, 103, 243–248).—A formula has been deduced

from which the mean value of the space-filling number of any substance, in the solid or liquid state, can be calculated. If  $\phi$  be the ionic volume calculated from the ionic mobility and  $V$  the volume derived from density determinations or by Kopp's formula, the space-filling number is given by  $\phi/V$  (compare A., 1916, ii, 311, 312). For a variety of ions, the space-filling number  $\phi/V_0$  referred to absolute zero on the empirical scale of corresponding states has a mean value of 0.4668. It is shown that the relation between volume and temperature can be expressed by an equation of the form  $V/V_s = a \cdot T/T_s + b$ , where  $s$  denotes the boiling point. From this it follows that  $\phi/V = \phi/V_s(a \cdot T/T_s + b)$ . For solids,  $a = 0.214$ ,  $b = 0.709$ , and for liquids  $a = 0.453$ ,  $b = 0.546$ . Since  $\phi/V_0 = 0.4668$ , and  $V_0/V_s$  has a mean value = 0.709,  $\phi/V_s = 0.331$ . Hence  $\phi/V = 0.331/a \cdot T/T_s + b$ . An equation of state is thus derived in which the space-filling number appears as a function of temperature.

E. H. R.

**Atomic Structure on the Basis of Atomic Disintegration and its Relationship to Chemical Linking, to Chemical Valency, and to the Electrochemical Character of the Elements.** EMIL KOHLWEILER (*Zeitsch. physikal. Chem.*, 1918, 93, 1—42).—The author describes a theory of the structure of the atoms built up on the radioactive theory; by means of this theory, he explains the existence of atomic weights which differ from whole numbers by the assertion that such atomic weights are due to the presence of isotopes in the material examined. The abnormalities of the periodic system are explained in the same way; for example, iodine and tellurium are both mixtures of two isotopes of atomic mass 126 and 128 respectively, but in different quantities. The position of the triads of group VIII of the periodic system is explained as due to the similarity of the positive charge with dissimilarity of the masses of the middle zone and different stability of the exterior electron system. On the basis of this relationship, the author draws relationships between the structure of the atom and the valency and method of linking, to the change in valency, dissociation, and the electric charge of the atom, and to the relationship between the electrochemical character and the valency of the elements. The tendency of certain elements to act with one valency in preference to another is also considered. For details of these points, the original must be consulted.

J. F. S.

**The Definition of the Term "Chemical Element."** RUD. WEGSCHEIDER (*Zeitsch. physikal. Chem.*, 1918, 92, 741—749).—A theoretical discussion based on the definition of an element put forward by Paneth (A., 1916, ii, 240). It is asserted that this definition in no way corresponds with that of most chemists, who retain the old definition as sufficient to express the chemical idea of an element.

J. F. S.

**Definition of the Term "Chemical Element."** FRITZ PANETH (*Zeitsch. physikal. Chem.*, 1918, 93, 86—88).—An answer

to Wegscheider's criticism (see preceding abstract) of the author's paper on this subject (A., 1916, ii, 240). J. F. S.

**Tables of Elements and Atoms.** FRITZ PANETH (*Zeitsch. physikal. Chem.*, 1918, **92**, 677—684).—The author proposes to substitute the present atomic weight table by two tables, (1) a table of combining weights containing those elements of which no isotopes exist, and using as combining weights the experimentally determined atomic weight, and (2) an atom table containing the whole of the elements, including all the isotopes with their theoretical atomic weights. The reasons for the proposed change are threefold: (1) There are more kinds of atoms than elements, (2) the combining weight of some elements is not the same as the atomic weight, and (3) in many cases there is no experimental confirmation of perfectly sound atomic weights which have been deduced from theoretical considerations. J. F. S.

**Twenty-fifth Annual Report of the Committee on Atomic Weights. Determinations Published during 1917.** GREGORY PAUL BAXTER (*J. Amer. Chem. Soc.*, 1918, **40**, 1009—1014).—These comprise hydrogen, helium, carbon and sulphur, bromine, zirconium, tellurium, and samarium. Only in the case of zirconium has evidence been presented during the past year which seems to demand an important alteration in the previously accepted atomic weight. By conversion of the tetrachloride into the dioxide, Venable and Bell have obtained the value 91.76 for the atomic weight of zirconium (A., 1917, ii, 479), which is more than a unit higher than the value given by the International Committee on Atomic Weights. C. S.

**The Periodic System and Genesis of the Elements.** CURT SCHMIDT (*Zeitsch. anorg. Chem.*, 1918, **103**, 79—118).—The author's hypothesis of the genesis of the elements (A., 1911, ii, 198) has been considerably amplified. The elements do not belong to a single system, but to four partial systems genetically connected. The primary or hydrogen system is only represented by hydrogen, which is regarded as the sole survivor of a past evolutionary period of matter. In it, the metallic and metalloid properties of matter have not become differentiated. Baur, from a study of logarithmic atomic volume curves, drew the conclusion that two different generations of elements can be distinguished (A., 1911, ii, 480). These two generations practically correspond with the author's secondary or helium partial system, comprising the elements He—Ti, As—Zr, Sb—Ce, Bi—Th, and the tertiary or iron system, comprising the remainder of the elements, with the exception of the rare earth metals, which form a distinct quaternary system. When this hypothesis is adopted, the problem of the double periodicity of the elements disappears; for instance, the metals copper, silver, and gold no longer appear in the same group as the alkali metals, since the former belong to the tertiary, the latter to the secondary partial system. The inert gases appear as the central group of the He



system with valency=0, contravalency= $\pm 8$ , whilst the iron, palladium, and platinum triplets occupy a corresponding position in the tertiary system, with maximum valency= $\pm 8$ , contravalency=0. The three blank spaces with which the He system begins are identified with elements detected spectroscopically in the nebulae and the hottest fixed stars. These, with their probable atomic weights, are nebulium, the parent of nitrogen, Nu, 1.31 or 1.63; eka-oxygen, Eo, 2.36; and eka-fluorine, Ef, 2.95.

Two principles are postulated, according to which the elements have probably been evolved: (1) the ontogenetic principle, involving the formation of the primary members of the different groups by direct condensation of protyl; (2) the phylogenetic principle, by which the higher members of the groups are developed from the lower by a process of integration. Evolution has taken place, not horizontally through the series, but vertically through the groups, each member of a horizontal series being independent of its neighbours. It follows that the atomic weights of potassium and argon, and of tellurium and iodine, present no anomaly. Some hitherto puzzling stellar phenomena also find their explanation in these principles; for instance, the occurrence of calcium and magnesium in certain stars which do not reveal the presence of oxygen and other elements of low atomic weight. The hypothesis is also in agreement with the relative abundance and distribution of the elements on the earth, and explains the frequent occurrence together of consecutive elements of the same group, such as zinc and cadmium. The direction of evolution was certainly from simpler to higher forms, following the course of cosmic evolution, and it is probable that, in atomic as in biological evolution, a process of selection with the survival of the fittest has been operative. There have probably been formed from time to time elements which, not being adaptable to the prevailing cosmic conditions, have undergone transformation. The radioactive elements are probably examples of such unsuitable types, and are at present passing through an evolutionary stage.

A rational system of nomenclature for the radioactive elements and their degradation products is suggested. Radium emanation is given the name *Radon*, Ro, which at once indicates its origin and its relationship to the argon group. The other emanations become *Thoron*, To, and *Acton*, Ao, respectively. The other degradation products are given names indicative of their derivation, manner of formation, and of the group of isotopes to which they are related. Thus radium-D becomes  *$\beta$ -radiotrilead*, with the symbol  $\beta$ -Ro<sup>'''</sup>Pb, and radium-C<sub>2</sub> becomes  *$\beta$ -radiotrithallium*,  $\beta'$ -Ro<sup>'''</sup>Tl, the accented  $\beta$  indicating that the product does not belong to the principal radium series, but to a side-chain. A complete list of new names for all the known products from uranium, actinium, and thorium is given.

E. H. R.

**New Table of the Periodic System.** INGO W. D. HACKH  
(*J. Amer. Chem. Soc.*, 1918, 40, 1023—1026).—Arranged in

vertical rows on either side of the central column of the non-valent elements are, on the right-hand side, the elements of the groups 1A, 2A, 3A, and 4 in the upper half of the table, and those of groups 1B, 2B, 3B, and 4 in the lower half, and, on the left-hand side, the elements of the groups 7A, 6A, 5A, and 4 in the upper half, and those of 7B, 6B, 5B, and 4 in the lower half. The elements of group 8 appear in the middle of the lower half of the table. This arrangement of the elements shows (1) a sharp classification of the elements into non-metals, noble gases, light metals, and heavy metals; (2) only five gaps, indicating that only five elements remain to be discovered; (3) elements having high electro-potential, simple spectra, and colourless ions appear in the upper half of the table, whilst those having low electro-potential, complex spectra, coloured ions, and tendency to form complex salts appear in the lower half; (4) on the left side of the table are the electronegative elements, those of the upper half forming strong acids, those of the lower half weak oxy-acids; on the right side of the table are the electropositive elements; (5) the middle of the lower half of the table is occupied by the amphoteric elements.

A peculiarity of the table is that the similarity of the elements is in the vertical direction in the upper half of the table and in the horizontal direction in the lower half.

C. S.

**Progress of Chemistry during the Past One Hundred Years.** HORACE L. WELLS and HARRY W. FOOTE (*Amer. J. Sci.*, 1918, [iv], **46**, 259—302).—A brief account is given of the general lines of development of chemical knowledge during the last hundred years.

H. M. D.

**New Filters.** R. ZSIGMONDY and W. BACHMANN (*Zeitsch. anorg. Chem.*, 1918, **103**, 119—128).—A new type of filter is described, termed a membrane filter, prepared by drying, under conditions not specified, solutions of certain colloids. The membranes thus obtained have a parchment-like appearance and a smooth surface, and are strong and durable. They can be prepared of any desired thickness and with any desired size of pore. The filters are very rapid in action and are particularly suitable for vacuum filtration, as they will stand high pressures. The membrane chosen for any particular filtration should be such that the pores are smaller than the diameter of the particles to be filtered. Under these conditions, no adsorption takes place, the pores do not get choked, and the membrane can be washed and used again with undiminished filtration velocity. A filter which, under 70 cm. pressure and with an area of 80 sq. cm. will pass 100 c.c. of water in eight seconds (an 8 sec. filter), will filter completely a graphite sol in which the particles are 200—300  $\mu\mu$  in diameter. A similar membrane will also stop gold particles of 80—100  $\mu\mu$ , but allows particles 30—40  $\mu\mu$  to pass through.

The membranes can also be used for separating the constituents of a mixed colloidal solution. Thus when a solution containing

Prussian blue and benzopurpurine was filtered through a 5 sec. filter (a relatively coarse membrane), the former was stopped completely, whilst the latter passed through. This was collected completely on a 3 min. filter. It is anticipated that the new filters will be valuable for many laboratory and technical purposes.

E. H. R.

### Inorganic Chemistry.

#### The Influence of Different Modifications of Sulphur on the Melting Point of Sulphur.

ERNST BECKMANN, RUDOLF PAUL, and OTTO LIESCHE (*Zeitsch. anorg. Chem.*, 1918, 103, 189—206).—The "natural freezing point" of sulphur,  $114.5^{\circ}$ , is  $4.75^{\circ}$  below that of normal sulphur,  $S_8$ . Assuming that the depression of the freezing point is due to the presence of  $S_2=128$ , the cryoscopic constant of sulphur being 213 (this vol., ii, 218), the proportion of  $S_2$  present must be 2.78%. This is in good agreement with Aten's conclusions, but not with that of Smith and his co-workers, who decided that "natural" sulphur contains about 3.6% of amorphous sulphur,  $S_n$ . The conclusion that "natural" sulphur does not contain  $S_2$  is also supported by the results of experiments on the effect of the addition of various forms of sulphur to sulphur of f. p.  $114.5^{\circ}$ , the additions being made to samples prepared under standard conditions, at a temperature just above the melting point. Amorphous sulphur, prepared in a variety of ways, has practically no effect on the freezing point, and is shown to be rapidly transformed into a mixture of  $S_8$  and  $S_2$  of the same composition as the fused mass. If the fusion is rapidly cooled after the addition of the  $S_n$ , only about 24% of the added sulphur is still insoluble in carbon disulphide. When added to a fused mass having a lower f. p. than  $114.5^{\circ}$ ,  $S_2$  has no effect, but when added to one having a higher f. p., it has the effect of lowering it towards the "natural" f. p., indicating that at the higher temperature relatively more  $S_2$  is formed from the  $S_n$ .

When  $S_n$  is heated, it shows no sharp melting point, but, having reached  $120^{\circ}$ , it has at once the "natural" freezing point  $114.5^{\circ}$ . If a mixture of rhombic sulphur with about 5%  $S_2$  is melted, it has a freezing point about  $2^{\circ}$  lower than that of a sample of rhombic sulphur similarly treated, indicating that under these conditions the  $S_n$  decomposes into 23%  $S_2$  and 77%  $S_8$ .

A sample of  $S_2$  prepared according to Aten's method (A., 1915, ii, 254) when added to a sample of "natural" sulphur lowered the f. p. slightly, indicating, however, only about 4.6%  $S_2$  in the preparation. Both rhombic and monoclinic sulphur raise the f. p. of "natural" sulphur by increasing the proportion of  $S_8$ .

A sample of Engel's sulphur,  $S_n$ , having a molecular weight of

192, was found to lower the f. p. of natural sulphur, but owing to the rapidity with which it decomposes, only 73% of the calculated depression could be observed. The decomposition of this form of sulphur is not a simple unimolecular reaction, and  $S_8$  appears to be an intermediate product.

E. H. R.

**Flame Reactions.** JACOB PAPISH (*J. Physical Chem.*, 1918, **22**, 430—432).—When the vapour of selenium dioxide is introduced into a Bunsen flame, an intense blue colour is produced. Elementary selenium is deposited on a cold surface which is brought into the blue flame. In similar circumstances, the vapour of tellurium dioxide produces a blue-coloured flame tinged with green in its uppermost part, and a bright, metallic mirror is deposited on a cold surface held in the hottest part of the flame. The reduction of the oxides in the flame is supposed to be the cause of the characteristic luminescence.

H. M. D.

**Occurrence of Hydrogen Selenide in Rain and Snow.** TH. GASSMANN (*Helvetica Chim. Acta*, 1918, **1**, 52—54).—One hundred c.c. of rain are concentrated to 80 c.c., and a strong current of sulphur dioxide is passed through the liquid for fifteen minutes. On keeping over night, a reddish-brown precipitate forms, which is shown to be selenium in the following way. It is oxidised with aqua regia and the solution precipitated with hydrogen sulphide; the precipitate is dissolved in fuming nitric acid, and the selenium precipitated either by hydrochloric acid or stannous chloride. Snow may be similarly treated.

Selenium may also be detected by precipitating the concentrated rain or snow water with a concentrated solution of barium chloride. The precipitate is collected after keeping over night, washed with ether, and dried in a desiccator over soda-lime. On treatment with concentrated hydrochloric acid, hydrogen selenide is evolved, which blackens a lead acetate paper.

It is probable that hydrogen selenide is not present as such in the rain or snow, but is in combination with a second component which has not yet been identified.

T. S. P.

**A New Oxide of Selenium.** FRITZ VON KONEK (*Ber.*, 1918, **51**, 872—876).—When diantipyryl selenoselenide,  $R_2Se \cdot Se$  (this vol., i, 407), was burnt in a bomb in oxygen under 25—30 atm. pressure, with the idea of converting the selenium into selenic acid, a white, amorphous deposit was found adhering firmly to the walls of the crucible. This proved to be an oxide, approximating to the formula  $Se_3O_4$ , which is almost insoluble in water, and is decomposed by boiling sodium hydroxide, about one-third of the selenium being deposited in the free state, the remainder giving rise to sodium salts of selenium acids. Strange to say, diantipyryl monoselenide, and diselenides of the type  $R \cdot Se \cdot Se \cdot R$ , provided by Lesser (A., 1912, i, 642) and Bauer (A., 1913, i, 263), gave no trace of this oxide.

J. C. W.

**Nitrogen Chloride, with a Convenient Method for its Preparation.** HASHMAT RAI (*Chem. News*, 1918, 117, 253).—About 10 c.c. of a freshly prepared, filtered, concentrated solution of bleaching powder in a large test-tube are cooled in ice to about  $0^{\circ}$ , and an equal volume of cold, saturated ammonium chloride solution is added. When the vigorous reaction has subsided, after ten minutes, the nitrogen chloride is exploded by the addition of turpentine. The chloride on the surface explodes instantly, that at the bottom more violently after some time, the interval between the two explosions depending on the height of the liquid column, the amount of turpentine added, the nature of the surface explosion, and the amount of nitrogen chloride present. All apparatus must be absolutely free from grease and direct sunlight should be entirely excluded. C. S.

**Catalytic and Thermal Syntheses of Ammonia.** E. B. MAXTED (*J. Soc. Chem. Ind.*, 1918, 37, 232–235r).—The author discusses the effect of the time of contact, temperature, and pressure on the percentage of ammonia formed and on the yield per litre of catalyst space in connexion with the catalytic synthesis of ammonia. Experiments are described on the thermal synthesis of ammonia at arc temperatures. J. F. S.

**Determination of the Surface Tension and Critical Density of Ammonia.** ALFRED BERTHOUD (*Helvetica Chim. Acta*, 1918, 1, 84–87).—The critical density of anhydrous ammonia has been determined by Young's method, as modified by Ter-Gazarian, the densities of the liquid and vapour being measured between  $0^{\circ}$  and the critical temperature,  $132.3^{\circ}$ . The critical density ( $d_c$ ) is found to be 0.2362, whereas the calculated value, ( $d_h$ ), assuming that the gas laws hold up to the critical point, is 0.05609. The ratio of  $d_c$  to  $d_h$  is 4.211, whereas the value of this ratio for normal liquids is approximately 3.6. This indicates that ammonia is associated even at the critical point, and the association is confirmed by measurements of the surface tension;  $K$ , in the Eötvös-Ramsay formula, is found to be 1.80 between  $11^{\circ}$  and  $59^{\circ}$ , giving a value of 1.27 for the association factor. Trouton's rule also gives a value of 23.8, which is higher than the normal value for unassociated liquids. T. S. P.

**Reduction of the Oxides of Nitrogen to Ammonia. Stability of Nitric Oxide.** PH. A. GUYE and FRITZ SCHNEIDER (*Helvetica Chim. Acta*, 1918, 1, 33–52).—In Switzerland, the conditions are such that oxides of nitrogen can be manufactured more conveniently than ammonia, so that a knowledge of the conditions under which the former are reduced to the latter becomes necessary. The authors have carried out such an investigation, using a special apparatus in which known mixtures of hydrogen with the respective oxides of nitrogen were passed over heated

reduced nickel as catalyst. The ammonia formed was estimated by absorption in a known volume of standard sulphuric acid. In some cases, this estimation was controlled by heating the solution with excess of sodium hydroxide and again absorbing the ammonia in standard acid; this was necessary in the case of nitrogen peroxide, since some ammonium nitrate is forming during the reduction.

In order to be quite certain of the results obtained, it was necessary to carry out preliminary experiments on the action of heat alone on some of the oxides of nitrogen used, since the statements found in the literature on this subject are somewhat contradictory and often have reference to the results obtained when the gas is heated under pressure. An apparatus was used in which the gas could be heated under atmospheric pressure, since the experiments on reduction were carried out at this pressure. It consisted of a cylindrical glass bulb heated in an electric furnace. Sealed on to the bottom of the bulb was a narrow glass tube, which could be cooled in liquid air or other cooling medium; products such as nitrogen peroxide could then be frozen out and identified.

In order to decompose nitric oxide under atmospheric pressure, it is necessary to raise the temperature to  $575^{\circ}$  and keep it there for several hours, even in the presence of spongy platinum as catalyst. Under these conditions, and contrary to what takes place under pressure, there is no formation of nitrous oxide. The primary products of decomposition are nitrogen and oxygen; on cooling, the oxygen reacts with undecomposed nitric oxide to give nitrogen peroxide. Nitrous oxide decomposes simply into nitrogen and oxygen.

In the reduction of the oxides  $\text{NO}$ ,  $\text{N}_2\text{O}$ , and  $\text{NO}_2$  by hydrogen, with nickel as catalyst, two reactions take place simultaneously, the one giving ammonia and the other nitrogen; for example,  $2\text{NO} + 5\text{H}_2 = 2\text{NH}_3 + 2\text{H}_2\text{O}$ ,  $2\text{NO} + \text{H}_2 = \text{N}_2 + \text{H}_2\text{O}$ . Both in the reduction of nitric oxide and of nitrogen peroxide, the formation of intermediate products, namely, nitrous oxide and nitric oxide respectively, does not occur.

In all these reactions, the condition of the reduced nickel plays an important part, and two different preparations do not necessarily give the same results. Also there is an optimum yield of ammonia which depends on the composition of the gaseous mixture and on the velocity with which the gases are circulated over the nickel.

Temperatures of  $250$ – $300^{\circ}$  appear to be the best for the formation of ammonia. Below these temperatures, the reduction takes place slowly, whilst above these temperatures, the nickel gradually loses its activity and the ammonia is appreciably decomposed into its elements.

Nitric oxide gives the best yields, 70% of the gas, on an average, being transformed into ammonia; 25–39% of nitrogen peroxide and only 3–7% of nitrous oxide is reduced to ammonia.

The reduction of the oxides of nitrogen to ammonia does not therefore appear to be an advantageous process from the manu-

facturing point of view, except perhaps in the case of nitric oxide, where a more systematic study of the conditions may give better results.

T. S. P.

**The Revision of the Atomic Weight of Carbon from the Densities of Acetylene, Ethylene, and Ethane.** KNUT STAHRFOSS (*J. Chim. phys.*, 1918, 16, 175—200).—The values obtained for the weight of a normal litre of gas are: for acetylene, 1.1791 grams; for ethylene, 1.2610 grams; for ethane, 1.3565 grams. From these, the atomic weight of carbon is calculated as 12.00, but this value will be subject to revision when it has been possible to determine directly the departure from Avogadro's law in the case of these gases, and when new determinations of the density of ethylene have been made.

W. G.

**Ultra-microscopic Investigation of very thin Metal Films obtained by Evaporation in High Vacuum. II.** W. REINDERS and L. HAMBURGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, 20, 1135—1154. Compare A., 1917, ii, 405).—The thin films of metal which are deposited on a glass surface when various metals are strongly heated in a highly exhausted space have been examined according to the method previously described (*loc. cit.*). It is found that elements which melt at high temperatures, such as tungsten, molybdenum, platinum, nickel, iron, and carbon, give rise to films which under the ultra-microscope are either entirely or for the most part devoid of structure. Elements of lower melting point show, on the other hand, a tendency to form films which have a clearly recognisable structure with ultra-microns as the structural units. The elements belonging to this group which have been examined are silver, gold, copper, magnesium, zinc, and cadmium. When the temperature of the glass surface on which the metal vapours condense was cooled by means of liquid air, the silver, copper, and gold films obtained were similar to those of the elements of high melting point in the first group. The lowering of the temperature of the condensing surface did not, however, eliminate the structural characteristics from the films of magnesium, zinc, and cadmium, although the coarseness of the structure was considerably reduced. The films devoid of structure show distinct signs of heterogeneity when the temperature is raised, this effect being very clearly marked in the case of films of silver, gold, platinum, iron, and molybdenum.

The films produced by tungsten, molybdenum, platinum, nickel, and iron are colourless, whilst those obtained from the other metals examined are coloured. That this colour does not depend on the structure or absence of structure is shown by the fact that the films of copper, silver, and gold have the same colour, whether these films are structureless or are ultra-microscopically heterogeneous. The colour effect is consequently due to the selective absorption of the atoms and is a characteristic property of the metal.

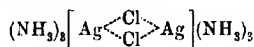
H. M. D.

**A Complete Review of Solutions of Oceanic Salts. IV.** ERNST JÄNECKE (*Zeitsch. anorg. Chem.*, 1918, **103**, 1—54. Compare this vol., ii, 70).—The influence of temperature on the equilibrium of the system  $(\text{Na}_2\text{--K}_2\text{--Mg})(\text{Cl}_2\text{--SO}_4)$  is given a graphic representation by the method developed in previous papers. The numerous diagrams given are fully explained in the paper.

E. H. R.

**The Nature of Subsidiary Valencies. XIX. Ammines of Silver.** FRITZ EPHRAIM (*Ber.*, 1918, **51**, 706—710).—The vapour tensions of the triammines of some silver salts have been measured by the author's usual method. A few of the compounds had only recently been prepared by Bruni and Levi (*A.*, 1916, ii, 482), whilst others had long been known. The following list gives the temperatures at which the vapour tensions of the triammines are 760 mm.: perchlorate,  $79.5^\circ$ ; chlorate,  $65.5^\circ$  (by extrapolation; highest reading,  $51.5^\circ$ ); chloride,  $17.7^\circ$ ; bromide,  $3.7^\circ$ ; bromate,  $1^\circ$ ; permanganate,  $12^\circ$ ; nitrate,  $63^\circ$ ; nitrite,  $69.3^\circ$ . The iodide, iodate, and periodate form no triammines.

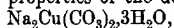
When the acid radicle is truly anionic, it is usually found that the stability of the ammines rises from chlorides to iodides and from chlorates to iodates. The complete reversal of this order in the case of the silver salts suggests, therefore, that there is a complex cation present, at any rate in the solid compounds, as expressed, for example, in the formula



J. C. W.

**The Crystal Form of Barium Iodide Hexahydrate.** O. MÜGGE (*Centr. Min.*, 1918, 105—107).—Commercial barium iodide crystallises at the ordinary temperature in large, hexagonal prisms without distinct end faces. The crystals are apparently isomorphous with  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ . The prism faces show diagonal striation always in the same direction on all faces of all crystals. The crystal class is probably trapezohedral tetartohedral;  $a:c = 1:0.538$  (approx.); double refraction fairly strong, negative. The crystals melt in their water of crystallisation at  $25.7^\circ$ . E. H. R.

**Double Carbonates of Sodium and Potassium with the Heavy Metals.** MALCOLM PERCIVAL APPLEBEY and KENNETH WESTMACOTT LANE (*T.*, 1918, **113**, 609—622).—An examination of the preparation and properties of the double salts



$\text{Na}_2\text{Co}(\text{CO}_3)_2 \cdot 4\text{H}_2\text{O}$ , and  $\text{K}_2\text{Co}(\text{CO}_3)_2 \cdot 4\text{H}_2\text{O}$  (compare Deville, *Ann. Chim. Phys.*, 1851, [iii], **33**, 75; Reynolds, *T.*, 1898, **73**, 262; Gröger, *A.*, 1907, ii, 240; Wood and Jones, *A.*, 1907, ii, 620; Luther and Kršnjavi, *A.*, 1905, ii, 705). The solubility equilibria are investigated for the sodium-copper and potassium-cobalt salts in the additional presence of the corresponding alkali hydrogen



carbonate, this being necessary in order to reduce the tendency to the separation of basic compounds.

For experimental details, reference should be made to the original. D. F. T.

**Utilisation of Waste Nessler Solution.** WILLIAM CLIFFORD (*J. Soc. Chem. Ind.*, 1918, **37**, 179r).—Nessler solution residues are treated with a few c.c. of sulphuric acid, whereby the mercuric iodide is precipitated. The mercuric iodide may be converted into sodium iodide as follows: 200 grams of the iodide are placed with 500 c.c. of water in a litre flask, and 20 grams of iron filings added. The mixture is heated for sixty minutes on a water-bath, when the reaction is complete, mercury being precipitated and ferrous iodide formed in solution. The green solution obtained by filtration is boiled and kept overnight, when it becomes ruby-red. The iron is then precipitated by sodium carbonate or hydroxide. Generally a second precipitation is necessary to remove all the iron. The filtrates from the second precipitation may be used directly for oxygen absorption determinations. Nessler solution may be prepared with sodium iodide and hydroxide just as well as with the potassium compounds. J. F. S.

**Ceric Oxychloride, produced in the Electrolysis of Cerous Chloride.** HANS ARNOLD (*Zeitsch. Elektrochem.*, 1918, **24**, 137—138).—When molten cerous chloride is electrolysed, a secondary reaction occurs at about 900° as long as there is an excess of water present in the molten mass. The product of this secondary reaction is a dark brown, amorphous powder which is deposited on the cooler parts of the anode. The product is very hygroscopic, and on analysis is shown to be a mixture of ammonium chloride, ceric oxychloride, and water. All attempts to remove the ammonium chloride by washing or sublimation converted the basic ceric chloride into cerous chloride. It is suggested that the product is produced from ceric chloride, formed on the anode, by the action of water, thus:  $\text{CeCl}_4 + \text{H}_2\text{O} = \text{CeOCl}_2 + 2\text{HCl}$ . The product always contains water, and analysis indicates that the water is combined and is present as  $\text{CeOCl}_2 \cdot 10\text{H}_2\text{O}$ . The compound is highly deliquescent and is hydrolysed by water with the formation of ceric hydroxide and cerous chloride. J. F. S.

**Carbides.** OTTO RUFF (*Zeitsch. Elektrochem.*, 1918, **24**, 157—162).—A preliminary paper on the temperature of formation and the stability range of carbides. The present paper deals with the equilibria between carbon and aluminium and between chromium and carbon. Aluminium carbide,  $\text{Al}_4\text{C}_3$ , sublimes at temperatures up to 2200° without melting and with some decomposition. This decomposition is independent of temperature. The melting point of aluminium carbide lies above this temperature. A vapour pressure curve has been constructed up to 2300°. At 2200°, aluminium carbide is in equilibrium with graphite,

aluminium saturated with graphite and vapour under a pressure of 400 mm. In the case of chromium and carbon, a composition-temperature diagram has been constructed for the pressure 10 mm. At 2270°, the mixture boils, and the vapour consists entirely of chromium. Between 2050° and 2250°, the fusion remains constant in composition and corresponds with  $\text{Cr}_3\text{C}_2$ . Below 2050° down to 1875°, graphite and the carbide,  $\text{Cr}_3\text{C}_2$ , exist side by side as solid phases. The compound  $\text{Cr}_3\text{C}_2$  is also shown to exist. J. F. S.

**The Determination of the Crystal Structure of Complex Compounds.** PAUL NIGGLI (*Physikal Zeitsch.*, 1918, 19, 225—234).

—The point system characteristic of any crystal can be determined from a knowledge of the crystal class and of the ratios of the distances between successive reflecting planes of atoms in the crystal in different directions as determined by the X-ray reflection method. As an example, the case of potassium alum, already examined by Vegard and Schjelderup (this vol., ii, 156), is worked out. The point system is the one designated  $T_h^2$ , and the elementary cube contains four molecules of the form  $[\text{Al}(\text{H}_2\text{O}_2)_6](\text{SO}_4)_2\text{K}$ . The aluminium, potassium, and sulphur atoms can be immediately identified with appropriate points in the point system. The oxygen atoms of the  $\text{SO}_4$  group appear to be of two kinds, three being alike, distributed symmetrically about a trigonal axis, the fourth being situated on the trigonal axis, and the four together forming a trigonal pyramid with the sulphur atom at the centre. The oxygen atoms of the water molecules probably correspond with two distinct groups of unfixed points in the system. The exact positions of the sulphur and oxygen points are not fixed by the symmetry of the system, but equations are developed by means of which their co-ordinates may be calculated when the relative intensities of the X-ray reflection spectra of different orders are known for the faces (100), (110), and (111). The author's solution of the alum structure differs to some extent from that put forward by Vegard and Schjelderup in the disposition of the oxygen atoms.

E. H. R.

**Crystal Structure of the Alums and the Rôle of the Water of Crystallisation.** CLEMENS SCHAEFER and MARTHA SCHUBERT (*Ann. Physik*, 1918, [iv], 55, 397—400).—Polemical.

The authors point out that the results of Vegard and Schjelderup (this vol., ii, 156) on the rôle of the water of crystallisation in the building up of the space grating of alums are not new, but were published by them in an earlier paper (A., 1916, ii, 505). A criticism of the spacial model of alums put forward by the same authors concludes the paper.

J. F. S.

**Basic Exchange in Permutite.** I. V. ROTHMUND and G. KORNFIELD (*Zeitsch. anorg. Chem.*, 1918, 103, 129—163).—The basic exchange which takes place between a hydrated alumin-

silicate such as permutite (compare Gans, A., 1914, ii, 55) and a neutral salt solution is to be regarded as a true chemical change and not as an adsorption phenomenon as suggested by Wiegner (A., 1912, ii, 981). In the case of permutite, an equilibrium rapidly becomes established with the solution. The resulting mixed permutite functions as a single solid phase, and is to be regarded as a solid solution, the composition of which depends on the relative concentrations of the cations in the solution. In the case of univalent cations, the composition of the permutite is independent of the total concentration of the solution, but when bivalent cations, for example, calcium, are present, the total as well as the relative concentration must be taken into account. The experimental work was confined to univalent metals, the equilibrium between silver permutite and the nitrates of potassium, rubidium, lithium, ammonium, and thallium, and between sodium permutite and ammonium and thallium nitrates, being investigated. If  $c_1$  and  $c_2$  represent the concentration of two bases in solution, and  $c'_1$  and  $c'_2$  their concentrations in the permutite in equilibrium with the solution, the empirical relation found is  $c'_1/c'_2 \cdot (c_2/c_1)^s = K$ , in which  $s$  is less than unity. The values of  $s$  and  $K$  vary considerably in the different cases examined. A bibliography of the subject of basic exchange is appended to the paper. E. H. R.

**Place of Manganese in the Periodic System.** F. RUSSELL VON BICHOWSKY (*J. Amer. Chem. Soc.*, 1918, 40, 1040—1046).—The arguments usually given for placing manganese in the seventh group are based on the periodic law, isomorphism, and chemical properties, and appear open to question in the light of modern knowledge. On the other hand, twelve different lines of argument based on purely chemical relationships are given by the author for placing manganese in the eighth group with iron, nickel, and cobalt. Moreover, the atom colours of the various valences of manganese show that the normal valence must be even, not odd (Bichowsky, this vol., ii, 142).

An improved form of the periodic table is presented showing the relations of the eighth and the rare earth groups to the rest of the periodic system. C. S.

**Structure of Tungsten Steels and the Change under Heat Treatment.** KŌTARŌ HONDA and TAKEJIRO MURAKAMI (*Sci. Rep. Tôhoku Imp. Univ.*, 1918, 6, 235—283).—Tungsten steels containing 0.12 to 1.57% of carbon and 0.23 to 30.0% of tungsten have been systematically investigated in respect of their magnetic susceptibility and micro-structure, and attention has been paid to the change of structure at high temperatures.

According to microscopic observations, the system iron-tungsten is characterised by the formation of a single compound,  $\text{Fe}_2\text{W}$ . The tungsten in tungsten steels may be present either in the form of iron tungstide or tungsten carbide, WC, or in both forms. The tungstide is soluble in iron to an extent represented by 9% of

tungsten, and in steels which contain a larger proportion of tungsten than corresponds with this limiting value the tungstide is present as a separate phase in globular form. As the carbon content increases, a larger proportion of tungsten is required for the appearance of the globules, this fact being due to the formation of tungsten carbide.

In the normal condition, the tungsten carbide is present in the form of the double carbide,  $4\text{Fe}_3\text{C}\cdot\text{WC}$ , which decomposes at  $400^\circ$ . At high temperatures, tungsten carbide reacts with iron in accordance with the equation  $\text{WC} + 5\text{Fe} = \text{Fe}_3\text{C} + \text{Fe}_2\text{W}$ , and when the steel is subsequently cooled, the transformation points are lowered by the dissolving of the iron tungstide in the iron.

The changes which occur under the influence of various methods of heat treatment are described in reference to a large number of magnetic susceptibility curves and photomicrographs. The authors consider that the occurrence of the double carbide,  $4\text{Fe}_3\text{C}\cdot\text{WC}$ , has been clearly proved by their investigations.

H. M. D.

**Adsorption Compounds. Ferriarsenites.** TADEUSZ ORYNG (*Kolloid Zeitsch.*, 1918, **22**, 149—154).—When a solution of a ferric salt is mixed with a solution of sodium arsenite and sodium hydroxide added to the mixture, a precipitate is obtained which contains ferric and arsenious oxides, and this has been regarded as an adsorption compound, the arsenious oxide being adsorbed by the precipitated ferric hydroxide. The systematic investigation of the composition of the precipitate in relation to that of the mother liquor has led the author to the conclusion that the facts cannot be satisfactorily explained in terms of the adsorption theory, and that the precipitate consists of a mixture of definite chemical compounds represented by the general formula  $x\text{Fe}(\text{OH})_3 \cdot y\text{As}_2\text{O}_3$ . In the author's opinion, many supposed cases of adsorption are probably examples of chemical changes of a similar type.

H. M. D.

**Peptisation of Ferric Arsenate and Phosphate and Formation of their Gels.** HARRY N. HOLMES and ROSSLENE ARNOLD (*J. Amer. Chem. Soc.*, 1918, **40**, 1014—1019).—A continuation of previous work (Holmes and Rindfusz, A., 1916, ii, 624). It is now found that unwashed precipitates of ferric arsenate or phosphate are stabilised by any soluble arsenates or phosphates that may be present, and therefore much more concentrated alkali hydroxide may be used as peptising agent, and it may be added more rapidly and in greater excess. The presence of thoroughly adsorbed alkali arsenate in precipitated ferric arsenate compels the use of more sodium hydroxide for peptisation, but the resulting colloid is stable in direct proportion to the amount of alkali arsenate present. Furthermore, if it is ammonium arsenate that is present in excess, less base is required for peptisation than in the case of other alkali arsenates, the order being  $\text{NH}_4$ , K, Na, Li. Ferric arsenate or phosphate can be peptised by sodium hydroxide or ferric chloride.

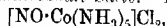
With sodium hydroxide, the action is greatly aided by sucrose or glycerol, but is hindered by sodium chloride. On dialysis of the colloids formed by the action of sodium hydroxide on ferric arsenate or phosphate, no gels form except in the presence of sucrose or glycerol.

Dialysis of the colloids formed by the ferric chloride peptisation of ferric arsenate or phosphate yields excellent gels. With barely enough ferric chloride for complete peptisation, the gels are opalescent and yellowish-grey, forming in a few days. With an excess of ferric chloride, the gels are red, weaker in structure, and slower in formation in direct proportion to this excess. Gels form in much less time when the original precipitate of ferric arsenate contains thoroughly adsorbed alkali arsenate; this accelerating influence of alkali arsenates decreases in the order  $\text{NH}_4 > \text{K} > \text{Na} > \text{Li}$ .

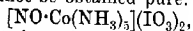
C. S.

**Nitrosopentamminecobalt Salts.** A. WERNER and P. KARRER (*Helvetica Chim. Acta*, 1918, 1, 54—78).—Sand and Genssler (A., 1903, ii, 549; 1904, ii, 39) have described two series of salts which they obtained by the action of nitric oxide on ammoniacal solutions of cobalt salts; the one series was red and the other black in colour, and both corresponded with the formula  $[\text{NO} \cdot \text{Co}(\text{NH}_3)_5]\text{X}_2$ . It was considered that the two series were valency isomerides, and the present authors have taken up the question again in order further to investigate the question of valency. They find that Sand and Genssler's statements with respect to the black series are correct, and some new salts are described, of which the iodate is very stable; most of the statements with respect to the red series are found to be incorrect.

**Black Nitrosopentamminecobalt Salts.**—The chloride,



is obtained by the method described by Sand and Genssler. In stoppered bottles it is quite stable, but on exposure to the air transformation to the red salt takes place, accompanied by partial decomposition. The transformation is due to moisture, and is not dependent on the action of light. The nitrate and sulphate are very unstable and cannot be obtained pure. The iodate,

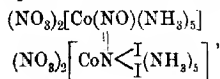


is precipitated almost immediately when nitric oxide is passed through a strongly ammoniacal solution of cobalt iodate, air being carefully excluded during the operation. It forms a blackish-brown, crystalline powder, and is quite stable in the absence of moisture. Attempts to prepare the bromide, iodide, cyanide, and chlorate were unsuccessful.

**Dinitrosodecamminedecobalt Salts (Red Salts).**  $\text{YX}_4$ , where  $\text{Y} = [\text{N}_2\text{O}_2 \cdot \text{Co}_2(\text{NH}_3)_{10}]$ .—The nitrate,  $\text{Y}(\text{NO}_3)_4$ , is obtained by Sand and Genssler's method, but the yields are very variable. It is best purified by precipitation from aqueous solution with sodium nitrate. When 20—25% nitric acid is added to the aqueous solution, an orange-coloured precipitate of the acid nitrate,  $\text{Y}(\text{NO}_3)_4 \cdot \text{HNO}_3 \cdot \text{H}_2\text{O}$ , is formed, which readily loses its water of crystallisation over

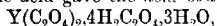
calcium chloride; over phosphoric oxide, some nitric acid also seems to be lost. The compound described by Sand and Genssler, namely,  $[Y(NO_3)_4 \cdot 2HNO_3] - H_2O$ , does not exist, nor could the pure additive products of the nitrate with silver nitrate and lead nitrate, described by these authors, be obtained.

The *acid perchlorate*,  $Y(ClO_4)_4 \cdot HClO_4 \cdot H_2O$ , falls as a reddish-brown powder when the cold, concentrated solution of the nitrate is precipitated with 30% perchloric acid solution. The compound  $[Y(ClO_4)_4 \cdot 2HNO_3] - H_2O$  does not exist. The compound



described by Sand and Genssler as being prepared by the action of potassium iodide and nitric acid on the nitrate could not be obtained. Probably a periodide is produced, which, however, is very unstable and cannot be obtained pure. By precipitation of a solution of the nitrate with potassium iodide, the *iodide*,  $YI_4 \cdot 4H_2O$ , is obtained as a brownish-yellow, flocculent precipitate; it is only obtained pure after several reprecipitations with potassium iodide. The compound,  $Y(NO_3)_2 \cdot I_2 \cdot KI$ , does not exist.

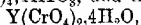
The double sulphate,  $Y(SO_4)_2 \cdot [N_2O_2 \cdot Co_2(NH_3)_6(OH_2)](SO_4)_2 \cdot 2H_2O$ , prepared by Sand and Genssler by the action of nitric oxide on an ammoniacal solution of cobalt sulphate, could not be obtained. The *sulphate*,  $Y(SO_4)_2 \cdot 2H_2O$ , was obtained from the nitrate by the aid of nitron sulphate; after collecting the nitron nitrate, the filtrate is precipitated with alcohol and ether. The compound,  $[Y(NO_3)_4 \cdot H_2SO_4] - H_2O$ , described by Sand and Genssler, could not be obtained, but by interaction of nitron sulphate with the nitrate, the *acid sulphate*,  $Y_2(SO_4)_4 \cdot H_2SO_4 \cdot 4H_2O$ , was prepared. The *bromide*,  $YBr_4 \cdot 3H_2O$ , is prepared by an analogous method to that used for the iodide, whilst the *acid bromide*,  $YBr_4 \cdot HBr \cdot H_2O$ , is obtained from the acid sulphate by the action of fuming hydrobromic acid. A chloride could not be obtained. Interaction of the nitrate and oxalic acid gave the *acid oxalate*,



as yellowish-brown needles, which on trituration with concentrated ammonia gave the *oxalate*,  $Y(C_2O_4)_3 \cdot H_2O$ , as long, dark red needles. The salts  $[(N_2O_2)_2 \cdot Co_2(NH_3)_6H_2O](SO_4)_4 \cdot 2H_2O$  and  $[Co_2(N_2OC_2O_4)(NH_3)_6H_2O](C_2O_4H)_4$

do not exist.

The *acid iodate*,  $Y(IO_3)_4 \cdot 4HIO_3$ , and the *chromate*,



are prepared from the nitrate by treatment with iodic acid and potassium chromate respectively. The former is a dark red, crystalline powder, and the latter an amorphous, yellowish-brown salt.

The above red nitrosopentamminecobalt salts must be considered as having the general formula  $(N_2O_2) \begin{array}{c} \text{Co}(NH_3)_5X_2 \\ \text{---} \\ \text{Co}(NH_3)_5X_2 \end{array}$ . Attempts to

decide the nature of the radicle  $\text{N}_2\text{O}_2$ , have not yet met with success. By the action of acids, the radicle is split off as  $\text{N}_2\text{O}_2\text{H}_2$ , which, however, immediately decomposes, giving  $\text{N}_2\text{O}$ ; the compound  $\text{N}_2\text{O}_2\text{H}_2$  could not be isolated or shown to be in solution, and statements made by Sand and Genssler that it is present in the solution obtained by the action of 68% nitric acid on the red nitrate are not correct. Since the compound  $\text{H}_2\text{N}_2\text{O}_2$  may be hyponitrous acid, attempts were made to synthesise the red salts by the action of silver hyponitrite on chloropentamminecobalt nitrate, but they were unsuccessful, aquopentamminecobalt salts being obtained.

T. S. P.

### The Solubility of some Metallic Hydroxides in Water.

GUSTAV ALMKVIST (*Zeitsch. anorg. Chem.*, 1918, **103**, 240—242).—The solubilities of the hydroxides  $\text{Ni}(\text{OH})_2$ ,  $\text{Co}(\text{OH})_2$ ,  $\text{BiO}(\text{OH})$ ,  $\text{Fe}(\text{OH})_3$ , and  $\text{MnO}(\text{OH})_2$  in water at  $20^\circ$  have been determined. As the results were required for analytical purposes, ordinary distilled water, not freed from carbon dioxide, was used. For the determination, the purified hydroxide was stirred for four days with water. About 2 litres of the filtrate were then evaporated to a small bulk, and the quantity dissolved was estimated gravimetrically, nickel and cobalt being weighed as sulphate after conversion of the hydroxide into sulphide, bismuth as  $\text{Bi}_2\text{O}_3$ . Iron and manganese, however, were determined colorimetrically. The following results were obtained per litre:  $\text{Ni}(\text{OH})_2$ , 12.7 mg.;  $\text{Co}(\text{OH})_2$ , 3.18 mg.;  $\text{BiO}(\text{OH})$ , 1.44 mg.;  $\text{Fe}(\text{OH})_3$ , 0.151 mg.;  $\text{MnO}(\text{OH})_2$ , 0.43 mg.

E. H. R.

### New Mixed Crystals and Compounds of Nickel Oxide with other Metallic Oxides.

J. ARVID HEDVALL (*Zeitsch. anorg. Chem.*, 1918, **103**, 249—252).—Experiments on the miscibility of nickel oxide with other oxides were made by fusing the mixed oxides together in varying proportions at about  $900^\circ$ , using potassium chloride as a flux. With magnesium oxide, homogeneous mixed crystals are formed within the limits 27—90% nickel oxide; outside these limits, it is difficult to distinguish microscopically between mixed crystals and the pure oxides. The mixed crystals are cubic and are intermediate in colour between the components.

With zinc oxide, homogeneous mixed crystals are formed when the zinc oxide is in excess. The crystals appear to be hexagonal, like those of Rinmann's Green. Probably a nickel zincate is formed which is miscible with excess of zinc oxide (compare A., 1914, ii, 133; 1916, ii, 331). The colours of mixed crystals of varying composition are not strictly proportional to their composition.

Homogeneous mixed crystals of nickel and manganese oxide were prepared with compositions ranging from  $\text{NiO}, 5\text{MnO}$  to  $5\text{NiO}, \text{MnO}$ . The crystals are slightly yellowish-green in colour and form octahedra and octahedral cubes.

Nickel oxide forms with alumina a blue compound,  $\text{NiO}, \text{Al}_2\text{O}_3$ .

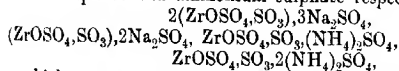
crystallising in small octahedra or octahedral cubes. Even a small excess of either oxide can readily be distinguished microscopically. The corresponding cobalt aluminate has been previously described (A., 1915, ii, 636).

With tin dioxide, nickel oxide reacts but slowly below 1000°, but a small quantity of a stannate analogous to cobalt stannate (A., 1915, ii, 638) appears to be formed. E. H. R.

**Colloidal Products of the Reactions between Potassium Dichromate and Stannous Salts.** J. C. WITT (*J. Amer. Chem. Soc.*, 1918, **40**, 1026—1030).—The phenomena observed when *N*-potassium dichromate is added to *N*-stannous chloride in equivalent proportions (Neidle and Witt, A., 1915, ii, 780; 1916, ii, 256; Neidle and Crombie, A., 1917, ii, 93) have been investigated. The mottled appearance is caused by a local excess of potassium dichromate; on keeping after the addition of an equivalent of dichromate, the remainder of the stannous chloride present gradually removed the dichromate from the precipitate, and the colloid was regenerated, producing a homogeneous, green liquid. A like precipitation of the colloids is produced by other electrolytes containing an anion having a valency greater than one. The reaction between stannous sulphate and potassium dichromate is essentially similar to that with the chloride. C. S.

**Zirconium Nitride.** P. BRÜERE and ED. CHAUVENET (*Compt. rend.*, 1918, **167**, 201—203).—The authors have prepared zirconium nitride by heating the tetra-ammonia derivative of zirconium chloride,  $ZrCl_4 \cdot 4NH_3$ , at 350°, and find that the product has the composition  $Zr_3N_4$ , and not  $Zr_2N_3$  as given by Wöhler (compare *Annalen*, 1839, **48**, 94) or  $Zr_2N_3$  as found by Mallet (*Amer. J. Sci.*, 1859, [ii], **28**, 346). The authors have repeated Wöhler's work, but are unable to confirm his formula. W. G.

**The Combinations of Acid Zirconyl Sulphate with some Alkali Sulphates (Na, NH<sub>4</sub>).** ED. CHAUVENET and (Mlle.) H. BUEYARD (*Compt. rend.*, 1918, **167**, 126—129. Compare this vol., ii, 269).—Thermochemical measurements indicate the existence of the following compounds of acid zirconyl sulphate with sodium sulphate and ammonium sulphate respectively:



which correspond to the following hydrates, which are stable in air at the ordinary temperature:  $2(ZrOSO_4 \cdot SO_3) \cdot 3Na_2SO_4 \cdot 8H_2O$ ,  $(ZrOSO_4 \cdot SO_3) \cdot 2Na_2SO_4 \cdot 7H_2O$ , and the trihydrate in the case of each of the double ammonium salts. Measurements have been made of the density, refractive index, and electrical conductivity of solutions of mixtures of varying proportions of the acid zirconyl sulphate and one of the alkali sulphates. In the case of mixtures with potassium sulphate, the formation of a precipitate prevented the making of exact measurements. W. G.



**Pure Antimony.** E. GROSCHUFF (*Zeitsch. anorg. Chem.*, 1918, **103**, 164—188).—Technically refined antimony is purer than electrolytic antimony prepared by the electrolysis of antimony sulphide solutions. The latter product when further refined gives a metal of a high degree of purity, containing less than 0.02% impurity. The different methods for purifying antimony and antimony compounds are reviewed. For the production of chemically pure antimony, the following process has been adopted. Antimony trichloride or pentachloride is purified by distillation, and is then transformed into the chlorantimonic acid,  $\text{SbCl}_4\text{H}_4\frac{1}{2}\text{H}_2\text{O}$ , described by Weinland and Schmid (A., 1905, ii, 326). This compound is specially adapted to the separation of antimony from all likely metallic impurities. After purification by recrystallisation, the chlorantimonic acid is readily hydrolysed to antimonic acid, which is reduced to metal preferably by melting with potassium cyanide. In a large preparation (about a kilogram) purified in this way, no impurities at all could be detected by qualitative methods. The melting point of the pure antimony is  $630.3^\circ$ .

Methods for the qualitative and quantitative analysis of nominally pure antimony are given. The solution of the antimony is effected in a variety of ways, according to the impurities present. The antimony is then converted into chlorantimonic acid, which is fractionally crystallised. The impurities are concentrated in the mother liquors, which are combined and analysed by the usual methods. Pure antimony dissolves completely in red, fuming nitric acid without evolution of gas. Under certain conditions of precipitation, antimonic acid is obtained in a sparingly soluble modification.

E. H. R.

**The Hydrates with  $3\text{H}_2\text{O}$  or  $n \times 3\text{H}_2\text{O}$ .** MARCEL DELÉPINE and PIERRE BOUSSI (*Bull. Soc. chim.*, 1918, [iv], **23**, 278—288).—A study of the dehydration of various platinichlorides, iridichlorides, and rhodochlorides containing 6 or  $12\text{H}_2\text{O}$  does not support Rosenstiehl's views (compare A., 1911, ii, 270, 386) on polymerised water and water of crystallisation.

W. G.

**The Acid Function of Osmium Tetroxide.** L. TSCHUGAEV (*Compt. rend.*, 1918, **167**, 162—163).—That osmium tetroxide has an acid function is shown by the fact that it forms definite compounds with the alkali hydroxides. The potassium compound,  $\text{OsO}_4 \cdot 2\text{KOH}$ , the rubidium compound,  $\text{OsO}_4 \cdot \text{RbOH}$ , and the two cesium compounds,  $\text{OsO}_4 \cdot \text{CsOH}$  and  $2\text{OsO}_4 \cdot \text{CsOH}$ , are all crystalline, of an orange or brown colour, and readily soluble in water, in which solution they are strongly hydrolysed. The compound  $[\text{Rh}_4\text{C}_6\text{H}_5\text{N}_2\text{Cl}_2]\text{OH} \cdot 2\text{OsO}_4$  was also obtained in the form of thin, yellow plates.

W. G.

## Mineralogical Chemistry.

### Boron, Lithium, and Thallium in Volcanic! Exhalations.

A. BRUN (*Bull. Soc. franç. Min.*, 1917, **40**, 107—110).—These elements may very often be detected spectrographically in the saline sublimations of fumaroles and in the altered scoria of Vesuvius and other volcanoes. Thallium was detected from Vesuvius, Etna, and Teneriffe in amounts ranging from 2.5 to 24 in 10,000. It is present as the soluble chloride in association with ammonium and sodium chloride, or as an insoluble sulphide in association with sulphides of arsenic.

L. J. S.

**Thallium in the Lead Sulpharsenate Minerals of the Binenthal, Switzerland.** A. BRUN (*Bull. Soc. franç. Min.*, 1917, **40**, 110—111).—Spectroscopic examination of crystals of sartorite, dufrenoyite, and jordanite, as well as all fragments giving a black or chocolate-brown streak, showed the presence of thallium. Hutchinsonite [which contains 5% of Tl] was not detected amongst these fragments. The association with sulphur and arsenic is here analogous to the Vesuvian occurrence.

L. J. S.

**Minerals from the Stanley Antimony Mine, Idaho.** EARL V. SHANNON (*Amer. Min.*, 1918, **3**, 23—27).—The ore consists of pure stibnite in a quartz-vein which carries some gold. The following mineral-species are described: stibnite, blende, gold, iron-pyrites, mispickel, kermesite, valentinite, cervantite, stibioferrite, and volgerite. The volgerite occurs abundantly as an earthy, dirty-white crust on stibnite; material from the interior of the crusts is more compact, somewhat translucent with a faint resinous lustre, and pale greyish-brown in colour. D<sub>20</sub> 3.082, H 3½. The mineral is completely soluble in hot concentrated hydrochloric acid, and at a red heat it gives off some oxygen, the higher oxide, Sb<sub>2</sub>O<sub>5</sub>, apparently passing into Sb<sub>2</sub>O<sub>3</sub>. It contains H<sub>2</sub>O 12.6, Fe<sub>2</sub>O<sub>3</sub> 1.4%. The amount of water is lower than that required by the usual formula (Sb<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O or Sb<sub>2</sub>O<sub>3</sub>·4H<sub>2</sub>O), but this may perhaps be explained by the colloidal nature of the material.

L. J. S.

**A peculiar Fibrous Form of Opal.** GEORGE P. MERRILL (*Amer. Min.*, 1918, **3**, 11—12).—Bunches of light gray, asbestiform material are embedded in a massive mixture of opal and chalcedony from Metolius, Oregon. It has the appearance of serpentine-asbestos (chrysotile), but is brittle and is harsh to the touch. Under the microscope it is seen to consist of wavy, colourless, isotropic fibres. Analysis gave: SiO<sub>2</sub> 89.56, Al<sub>2</sub>O<sub>3</sub> + Fe<sub>2</sub>O<sub>3</sub> 4.72; loss on ignition, 5.62%.

L. J. S.

**Ores of Manganese and Iron from the Crystalline Massif of Brosteni, Roumania.** V. C. BUTUREANU (*Bull. Soc. franç. Min.*, 1917, **40**, 164—177).—A résumé is given of previous papers (P. Poni, A., 1901, ii, 26; Butureanu, A., 1908, ii, 955; 1909, ii, 745; 1912, ii, 949). The minerals considered are manganites of manganese and iron (brostenites of Poni) and carbonates of manganese and iron (ponites of Butureanu). The brostenites have been derived by the alteration of the ponites. Numerous analyses are quoted showing the wide range in composition. L. J. S.

**Ulexite from Lang, California.** WILLIAM FOSHAG (*Amer. Min.*, 1918, **3**, 35).—This occurs in some quantity, associated with colemanite, howlite, and calcite, in the Sterling Borax Co. mine. It has a fibrous structure with a botryoidal surface; it differs from the ordinary type of this mineral in being more compact and harder ( $H=3\frac{1}{2}$ ) and in its association with colemanite. Analysis gave:

B <sub>2</sub> O <sub>3</sub>	CaO.	H <sub>2</sub> O.	Na <sub>2</sub> O.	Total.
43.13	14.14	35.68	[7.05]	100.00

The mineral is probably a lake deposit from the alkaline waters of the neighbouring streams, and the colemanite has perhaps been derived from it by the action of alkaline chloride solutions.

L. J. S.

**Randannite [= Diatomite] from Madagascar.** A. LACHOIX (*Bull. Soc. franç. Min.*, 1916, **39**, 85—88).—A bed of diatomite, interbedded with basaltic tuffs, is exposed on the banks of the stream Sandrangoty, near Mt. Raynaud, in the extreme north of Madagascar. The material is white, porous, and fairly coherent. Under the microscope, the material is seen to be colourless, colloidal, and to be composed of fusiform diatoms. Analysis by Raoult gave:

SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MgO.	CaO.
76.00	1.24	6.24	1.80	0.85	0.07	0.80
Na <sub>2</sub> O.	K <sub>2</sub> O.	P <sub>2</sub> O <sub>5</sub> .	H <sub>2</sub> O at 105°.	H <sub>2</sub> O (ign.).	Organic matter.	Total.
0.39	0.18	0.12	5.87	6.07	0.60	100.23

The high percentage of titanium dioxide suggests that the impurities (Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> [2.90%] insoluble in alkali) are due to the presence of admixed laterite. L. J. S.

**Lattice-like Inclusions in Calcite from North Burgess, Ontario.** R. P. D. GRAHAM (*Min. Mag.*, 1918, **18**, 252—258).—Pale blue, coarsely crystalline calcite from this locality shows twin-striations, due to repeated twinning on the obtuse negative rhombohedron  $c(110)$ , and encloses fine needles, which are arranged parallel to the edges of this rhombohedron. On dissolving the calcite in acid, these needles remain as a delicate and intricate network or lattice-like structure. Analyses of this material, D 25.

gave the results under I and Ia, agreeing with the formula  $5\text{MgO} \cdot 6\text{SiO}_2 \cdot 4\text{H}_2\text{O}$ . The material is slightly attacked by hydrochloric acid; after digestion with concentrated acid and drying at  $100^\circ$ , the residue had the composition given under II. The blue calcite itself (anal. III) contains very little magnesia.

	$\text{SiO}_2$	$\text{MgO}$	$\text{FeO}$	$\text{CaO}$	$\text{H}_2\text{O}$	$\text{CO}_2$	Total.
I.	57.23	30.35	1.66	0.37	n.d.	—	—
Ia.	56.37	30.43	2.47	nil	10.87	—	100.14
II.	63.93	26.16	1.21	—	8.08	—	99.38
III.	—	0.41	—	56.12	—	43.53	100.06

L. J. S.

**Mineralogy of Black Lake Area, Quebec.** EUGENE POITEVIN and R. P. D. GRAHAM (*Museum Bull. Geol. Survey Canada*, 1918, No. 27, 1—82).—An account is given of thirty-four mineral species found in the several asbestos (chrysotile) and chromite mines and quarries in the 'serpentine belt' near Black Lake, Megantic Co., Quebec. Many of these minerals are aluminosilicates rich in lime, such as idocrase, grossularite, etc., which are usually formed by the contact-metamorphism of impure limestones. In this area, however, they occur as fillings in dyke-like fissures penetrating peridotite and serpentine, that is, in rocks containing very little lime (0.20—0.68%  $\text{CaO}$ ). These dykes are considered to represent the last phase of the igneous intrusions, when the residual acid magma or magmatic waters became enriched in lime by their solvent action on the surrounding rocks. Analyses are given of the following minerals: I. Diopside, colourless crystals from the Montreal chrome pit. Corresponding with the low percentage of iron, the refractive indices ( $\alpha_n = 1.669$ ,  $\beta = 1.676$ ,  $\gamma = 1.698$ ) are lower than any previously recorded for diopside. II. Grossularite, colourless, transparent crystals from Southwark pit; refractive index, 1.734. III., lilac-coloured, and IV., yellowish-green crystals of idocrase; the refractive indices ( $\omega = 1.708$ ;  $\epsilon = 1.705$ ) of the lilac-coloured crystals are low. V.—VII. *Colerainite*, a new species, forming minute, colourless, hexagonal scales which are optically uniaxial and positive ( $n = 1.56$ ), and are often aggregated as white rosettes or botryoidal forms. Analysis V of the crystals leads to the formula  $4\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 5\text{H}_2\text{O}$ . Analyses VI and VII are of the underlying matrix, which is white, finely granular to compact, and resembles unglazed porcelain in appearance; this material

	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{FeO}$	$\text{MnO}$	$\text{CaO}$
I.	54.77	—	0.17	0.89	0.11	26.33
II.	39.49	22.35	—	1.00	0.15	36.62
III.	36.88	20.03	0.85	n.d.	0.23	37.61
IV.	36.62	15.96	4.30	0.54	trace	38.66
V.	24.40	22.77	0.45	n.d.	0.09	0.10
VI.	26.98	16.10	0.22	nil	0.20	0.12
VII.	33.00	13.12	—	—	—	trace
VIII.	43.31	0.38	0.27	nil	trace	0.12
IX.	50.29	6.23		1.00	—	nil
X.	48.88	3.56		1.36	—	nil

	MgO.	(K,Na) <sub>2</sub> O.	H <sub>2</sub> O.	Total.	Sp. gr.
I.	18.46	—	—	100.73	3.267
II.	0.28	—	—	99.89	3.60
III.	2.17	—	3.09	100.86	3.32
IV.	1.25	—	3.18	100.51	—
V.	32.70	0.30	19.63	100.44	2.51
VI.	36.56	0.28	19.91	100.37	2.44
VII.	35.30	0.26	18.67	100.35	2.34
VIII.	40.03	0.28	15.77	100.16	2.51
IX.	29.99	—	13.30	100.81	—
X.	31.41	—	15.67	100.88	—

consists mainly of the mineral colesrainite. VIII is of 'precious' or 'noble' serpentine from the Megantic mine; this is chrysoprase-green and translucent with a somewhat waxy or greasy lustre. Included in it are sometimes grains and veins of chromite and the rare mineral stichtite, a chromiferous magnesium hydroxy-carbonate. IX and X are of porcellophite, an impure variety of serpentine; IX is of pale grey material from the Megantic mine, and X, of pale brown material from the Hall chrome pit; both are very compact, resembling dried clay in appearance, and so light that they float on water.

L. J. S.

**Flokkite, a New Zeolite from Iceland.** KAREN CALLISEN (*Medd. Dansk Geol. For.*, 1917, 5, No. 9, 1—6).—A specimen in the Copenhagen Museum, labelled 'Eskefjord? Iceland,' and regarded as mesolite, proved on examination to represent a new species. It forms slender, flattened, monoclinic prisms with perfect (100) at (010) cleavages. The crystals are water-clear or pale yellowish-green. Sections perpendicular to the prism-zone show a division into sectors with different optical orientations.  $n_{\alpha} = 1.4720$ ,  $n_{\gamma} = 1.4736$ ; D 2.103; H 5. Before the blowpipe, the material fuses readily with intumescence; it is not attacked by hydrochloric acid. Analysis by C. Christensen gives the formula  $H_8(Ca,Na_2)Al_3Si_9O_{36}, 2H_2O$ .

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	Na <sub>2</sub> O.	H <sub>2</sub> O > 100°.	H <sub>2</sub> O < 100°.	Total.
67.69	12.43	2.65	0.09	4.36	8.82	4.53	100.57

L. J. S.

**The Mesosiderite-Grahamite Group of Meteorites:** Analysis of Vasca Muerta, Hainholz, Simondium, and Powder Mill Creek. G. T. PRIOR (*Min. Mag.*, 1918, 18, 151—172. Compare A., 1916, ii, 635).—In the Rose-Tschermak-Brezina classification of meteorites, the mesosiderites are defined as consisting of iron and crystalline olivine and bronzite, with the metallic and stony matter in approximately equal amounts, whilst the grahamites contain the same constituents with the addition of plagioclase-felspar. It is now found that typical members of both groups contain abundant felspar, and that there is no essential difference between them. For the combined group, the earlier name mesosiderite is retained. The members of this group consist mainly of pyroxene and felspar, with nickel-iron in large amount,

but rather unevenly distributed, and nodules of olivine somewhat sparsely distributed, but occasionally of considerable size. Accessory constituents are troilite, chromite, and schreibersite. The felspar is nearly pure anorthite; the pyroxene is fairly rich in iron, the ratio of  $\text{MgO}:\text{FeO}$  being about 2:1; the olivine, on the other hand, is poor in iron, the ratio  $\text{MgO}:\text{FeO}$  being from 6:1 to 10:1; and the nickel-iron is poor in nickel,  $\text{Fe}:\text{Ni}=10:1$  to 13:1. The cataclastic structure of the mesosiderites suggests that they represent a mixture of two types, to one of which belong the pyroxene and anorthite, and to the other the iron and olivine.

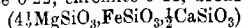
Vaca Muerta (Chili).—Several masses ('Sierra de Choca,' 'Llano del Inca,' 'Doña Inez,' etc.) are included in this fall. The bulk-composition (I) is deduced from analyses of the magnetically attracted portion and of the portions soluble and insoluble in hydrochloric acid of the unattracted portion. Ia is of the olivine, corresponding with  $10\text{Mg}_2\text{SiO}_4, \text{Fe}_2\text{SiO}_4$ , and Ib is the mineral composition. Hainholz (Westphalia).—II the bulk-composition, IIa of the olivine ( $7\text{Mg}_2\text{SiO}_4, \text{Fe}_2\text{SiO}_4$ ), and IIb the mineral composition. Simondium (Cape Colony) (A., 1910, ii, 315).—This is much weathered. The portion of the unattracted material soluble in water contained  $\text{NiO}$  1.28,  $\text{CaO}$  0.91,  $\text{SO}_3$  2.71%. Other detailed analyses are given. Powder Mill Creek (Tennessee).—The attracted portion contained  $\text{Fe}$  73.15,  $\text{Ni}$  5.61, insoluble 11.58, anorthite, etc. (9.66)=100. The olivine gave IIIa, corresponding with  $10\text{Mg}_2\text{SiO}_4, \text{Fe}_2\text{SiO}_4$ . The composition of some other meteorites of this group is also discussed.

Nickel-iron.			Troilite.		Schreibersite.							
Fe.	Ni.	Co.	Fe.	S.	Fe.	Ni.	P.	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	Cr <sub>2</sub> O <sub>3</sub> .	
I. 38.25	2.90	0.36	1.37	0.79	1.27	0.70	0.35	26.02	5.87	1.36	0.45	
II. 42.13	4.00	0.41	2.52	1.44	0.36	0.23	0.10	21.69	4.99	2.77	0.33	
FeO.			MnO.	NiO.	CaO.	MgO.	Na <sub>2</sub> O.	P <sub>2</sub> O <sub>5</sub> .	H <sub>2</sub> O.	Total.		
I. 7.03	0.24		—	4.35	7.36	0.18	—		0.54	99.39		
II. 6.19	trace		0.48	3.49	7.07	0.21	0.34		1.20	99.95		
SiO <sub>2</sub> .			FeO.		MgO.		Insol.		Total.			
IA.	39.89		8.98		49.50		1.95		100.32			
IIA.	40.48		11.59		42.97		2.76		97.80			
IIIA.	40.18		9.15		48.91		1.42		99.66			
Nickel-iron.			Troilite.		Anorthite.			Pyroxene.				
IB.	41½		2		17			32				
IIb.	46½		4		14½			27				
Olivine.			Chromite.		Rust.			Schreibersite.				
IB.	1½		1		2			3				
IIb.	1½		½		4			2				

L. J. S.

**Composition of the Meteorites Amana and Eagle Station.**  
G. T. PRIOR (*Min. Mag.*, 1918, 18, 173—179).—The Amana or Homestead meteoric stones, which fell in Iowa Co., Iowa, on

February 12th, 1875, were in the same year analysed by G. D. Hinrichs, J. L. Smith, and by C. W. Gumbel and Schwager. These analytical results show some discrepancies amongst themselves and are not in agreement with the author's theory of the genetic relationship of meteorites (A., 1916, ii, 635). The following new analysis was therefore made. The bulk-composition (I) deduced from analyses of the magnetically attracted portion and of the portions soluble and insoluble in hydrochloric acid of the un-attracted portion, agrees with the following mineral composition: feldspar 9.76, apatite 0.22, chromite 0.44, bronzite



30.75, olivine  $(3\frac{1}{2}\text{Mg}_2\text{SiO}_4, \text{Fe}_2\text{SiO}_4)$  40.15, nickel-iron 10.99, troilite 6.25, water 0.47%. This meteorite therefore contains about 11% of nickel-iron in which the ratio of Fe:Ni is 8:1, whilst the ratio of MgO:FeO in the ferromagnesian silicates is 4:1; it thus occupies an intermediate position between the type-meteorites Cronstad (C2) and Baroti (C3).

Nickel-iron.									
	Fe.	Ni.	Co.	Fe.	S.	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Cr <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .
I.	9.71	1.19	0.09	3.97	2.28	39.27	2.10	0.32	0.40
	FeO.	MnO.	CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	H <sub>2</sub> O.	P <sub>2</sub> O <sub>5</sub> .	Total.
I.	12.06	0.08	1.78	24.88	0.92	0.13	0.47	0.26	99.91.

A new analysis of the Eagle Station meteorite, which was found in 1880 in Carroll Co., Kentucky, gave II for the attracted portion and III for the olivine. These results confirm those of J. B. Mackintosh (1887). In the nickel-iron the ratio of Fe:Ni is about 6:1 (instead of more than 10:1, as in most other pallasites), and in the olivine the ratio of MgO:FeO is about 4:1 (instead of about 7:1). In composition, as well as in structure, this pallasite is thus exceptional; and it may perhaps be placed in the group A3 (A., 1916, ii, 635).

	Fe.	Ni.	Co.	SiO <sub>2</sub> .	MgO.	FeO.	P <sub>2</sub> S <sub>5</sub> &c.	Total.
II.	79.74	13.98	1.04	1.42	1.74	0.77	(1.31)	100.00
III.	—	—	—	39.22	42.31	18.83	—	100.36

L. J. S.

### Analytical Chemistry.

**Quinone-Phenolate Theory of Indicators. Absorption Spectra of Solutions of Phenolsulphonaphthalein and its Tetrabromo- and Tetranitro-derivatives and their Salts, and of Analogous Substances.** E. C. WHITE and S. F. ACREE (*J. Amer. Chem. Soc.*, 1918, **40**, 1092—1099).—Since phenolsulphonaphthalein and its derivatives and their salts furnish the best series of indicators yet found for acidimetry and for the study

of the quinone-phenolate theory (White, *Science*, 1915, **42**, 101; Lubs and Acree, A., 1917, ii, 97; Lubs and Clark, A., 1916, ii, 44, 570; White and Acree, A., 1917, i, 340), the authors intend to make a series of phenolsulphonethaleins covering a range of hydrogen-ion concentrations from  $10^{-1}$  to  $10^{-13}$  or more.

The following results are established in the present paper. The yellow colour and the absorption spectrum of phenolsulphonethalein solutions are not altered by the addition of alkali hydroxide up to 0.75 mol. When more alkali is added, the yellow colour changes to deep red, and there is a corresponding shift in the absorption band. This is interpreted as evidence that the intense red colour of the alkali salts of indicators of this series does not come from the non-ionised quinone-phenol group, but arises from the quinone-phenolate anion. In accordance with this conception, it is found that the introduction of negative bromo- and nitro-groups into the phenol nucleus increases the ionisation of the phenol group, increases the conductivity, lowers the  $P_H$  value, and gives to the solution a greater concentration of quinone-phenolate anions, and therefore increases the deep red colour and changes the position of the absorption band so as to cut out a part of the yellow. The addition of hydrochloric acid suppresses the ionisation of the phenol group and changes the deep red colour into the yellow of the quinone, and therefore shifts the absorption band so as to include less of the yellow.

The similarity of the absorption spectra of alkaline solutions of sulphonethaleins, phenolphthaleins, aurin, fluorescein, and related substances gives evidence that the deep red colour in all these cases arises from the presence of a quinone-phenolate anion.

C. S.

**Behaviour and Detection of the smallest Quantities of Carbon Monoxide in the Chlorate Pipette.** K. A. HOFMANN and HELGE SCHIBSTED (*Ber.*, 1918, **51**, 837—842. Compare A., 1916, ii, 636, 637).—It has already been emphasised that the rate at which hydrogen is absorbed in the "chlorate pipette" (sodium chlorate solution activated by osmium tetroxide; porous rods impregnated with platinum and a little palladium) is greatly lessened by traces of carbon monoxide. In order to render this influence most obvious, it is not advisable to consider the observed rate of absorption, for this depends on the surface area of the platinised tubes which reach out into the gas, and these become more and more immersed in the chlorate solution as the oxidation proceeds. The exposed surface is obviously proportional to the volume of gas left unabsorbed, for the tubes are arranged vertically in a cylindrical part of the apparatus, and therefore it is possible to arrive at the "relative rate of absorption." With pure hydrogen, this relative rate is constant, or slowly rises, until half the gas is absorbed, whilst traces of carbon monoxide cause a rapid fall in this rate. If the pipette is standardised and a curve is plotted connecting the relative rates of absorption at "half



volume" with various proportions of carbon monoxide, the phenomenon can be employed further for quantitative purposes.

J. C. W.

**Estimation of Chlorine in Urine.** EMIL VOTOČEK (*Chem. Zeit.*, 1918, **42**, 317—318).—Ten c.c. of the urine are diluted with water to about 160 c.c., 5 c.c. of nitric acid and 6 drops of sodium nitroprusside solution (0.6 gram of the salt in 3 c.c. of water) are added, and the mixture is titrated with *N*/10-mercuric nitrate solution until a turbidity develops; the turbidity, when the end-point is reached, should not disappear within less than two minutes.

W. P. S.

**Detection and Estimation of Bromine, especially in Mineral Waters.** JOSÉ CASARES and A. TASTET (*Anal. Fis. Quim.*, 1918, **16**, 226—228).—A modification of Guareschi's method of estimating bromine (A., 1912, ii, 1208) which enables 0.0002 gram of bromine per litre to be detected.

A. J. W.

**Volumetric Estimation of Sulphur in Pyrites and Slag.** ERNEST MARTIN (*Mon. Sci.*, 1918, [v], **8**, ii, 149—150).—The slag or pyrites is treated with aqua regia, the solution evaporated to dryness, and the residue redissolved in dilute hydrochloric acid. The solution is diluted, and sodium carbonate added. The assay may also be opened out by fusion with sodium peroxide or a mixture of sodium carbonate and potassium nitrate, dissolved in water, and carbon dioxide passed through to precipitate lead. After filtration, methyl-orange is added, and the solution exactly neutralised with hydrochloric acid. The carbon dioxide is boiled off, and to the luke-warm solution a known volume of standard barium hydroxide and phenolphthalein are added. Carbon dioxide is bubbled through until the colour just changes, when the solution is cooled and titrated with *N*/2-hydrochloric acid.

F. C. T.

**Estimation of Thiosulphuric, Sulphurous, Trithionic, and Sulphuric Acids in a Mixture.** O. BILLETER and B. WÄVRE (*Helvetica Chim. Acta*, 1918, **1**, 174—180).—The authors describe methods by which the above-named acids may be estimated in a mixture of all four. The total sulphur present is oxidised to sulphuric acid by warming with bromine water and the whole estimated as barium sulphate. The sum of the sulphite and thiosulphate is next estimated by titration with a standard iodine solution. The sulphite is then estimated alone by titration with a solution of sodium disulphide, according to the equation  $\text{Na}_2\text{S}_2 + \text{Na}_2\text{SO}_3 = \text{Na}_2\text{S} + \text{Na}_2\text{S}_2\text{O}_3$ .

The estimation is carried out in the presence of ammonium chloride at the boiling point, the end of the reaction being indicated by the persistence of the yellow colour of the standard solution. It is also advisable to circulate a current of carbon dioxide over the solution during titration.

Sodium trithionate reacts with sodium sulphide according to the equation  $\text{Na}_2\text{S} + \text{Na}_2\text{S}_3\text{O}_6 = 2\text{Na}_2\text{S}_2\text{O}_3$ , and consequently can then be estimated by a further titration with standard iodine. The reaction is carried out by boiling the solution with sodium sulphide for a few minutes, then adding sodium acetate and acetic acid and boiling to decompose excess of sulphide, and finally titrating with iodine. Should sulphite also be present, the thiosulphate titrated here will be made up (1) of that produced from the sulphite and (2) that produced from the trithionate, but as the amount due to the sulphite estimation is known, the calculation of the concentration of the trithionate follows. The method is very good, and in the estimation of the sulphite the end-point is emphasised by the appearance of a turbidity due to the liberation of sulphur. The amount of trithionate may be estimated by two other methods. (1) After the sulphite and thiosulphate have been titrated with iodine, sodium iodide is added and an excess of iodine, and the mixture heated under pressure; this oxidises the trithionate to sulphate. The same action occurs with the tetrathionate formed in the first estimation, and allowance must be made for this. After boiling for a few minutes, the flask is cooled and the excess iodine titrated with thiosulphate. (2) This method is based on the decomposition by trithionic acid according to the equation  $\text{H}_2\text{S}_3\text{O}_6 = \text{H}_2\text{SO}_4 + \text{SO}_2 + \text{S}$ . The mixture is acidified, and boiled while a current of carbon dioxide is passed through until all the sulphur dioxide has been expelled; the free sulphur is then filtered off and the sulphate estimated with barium chloride. This sulphate will represent 97.9—97.5% of the trithionate, and, of course, contains the sulphate originally present.

J. F. S.

[Analysis of Organo-selenium Compounds.] FRITZ VON KONEK and OSKAR SCHLEIFER (*Ber.*, 1918, 51, 852—855).—See this vol., i, 407.

**Micro-Dumas Estimation of Nitrogen in Liquids Poor in Nitrogen.** GEORG KRAEMER (*J. pr. Chem.*, 1918, [ii], 97, 59—60).—The micro-Kjeldahl method for estimating nitrogen in small quantities of liquids such as milk can be replaced satisfactorily by a micro-Dumas process working with approximately 0.25 c.c. [See also *J. Soc. Chem. Ind.*, 526A.]

D. F. T.

**The Estimation of Nitrogen by the Kjeldahl Method.** A. VILLIERS and (MLLE.) A. MOREAU-TALON (*Bull. Soc. chim.*, 1918, [iv], 23, 308—311).—The authors advocate the combination of the method in which potassium sulphate is used with that in which mercury is used. The substance is digested with potassium sulphate and sulphuric acid until colourless, and, after partial cooling, 1 gram of mercury is added, and the digestion is continued for a quarter of an hour after the mixture has boiled. The remainder of the estimation is carried out as usual.

W. G.

**The Estimation of Ammonia and Hydrochloric Acid by Weighing as Ammonium Chloride.** A. VILLIERS (*Bull. Soc. chim.*, 1918, [iv], 23, 306—308).—The author reaffirms the accuracy of his method (compare A., 1900, ii, 310) for the estimation of ammonia or hydrochloric acid by weighing as ammonium chloride. W. G.

**Estimation of Ammonia in Urine, Serum, etc.** H. WIESSMANN (*Landw. Versuchs.-Stat.*, 1918, 91, 346—352).—Distillation in the presence of dilute sodium carbonate solution at 50° and under 5 to 10 mm. pressure is recommended; urea does not yield any ammonia under these conditions. [See, further, *J. Soc. Chem. Ind.*, 532A.] W. P. S.

**Estimation of Nitrates and Nitrites.** WILHELM STRECKER (*Ber.*, 1918, 51, 997—1004).—Two well-known reactions are employed for the estimation of nitrites and nitrates in mixtures, namely, those represented by the equations  $\text{NO}_2' + \text{NH}_4' = \text{N}_2 + 2\text{H}_2\text{O}$  and  $\text{NO}_2' + 3\text{Fe}'' + 4\text{H}' = \text{NO} + 3\text{Fe}''' + 2\text{H}_2\text{O}$ . The solution to be analysed, containing nitrites and nitrates equivalent to not more than 0.11 gram  $\text{NaNO}_2$  and 0.18 gram  $\text{KNO}_3$ , is dropped into a boiling, concentrated solution of ammonium chloride, at least 100 times as much of this salt being taken as the nitrite present, the solution being in a flask which is provided with an apparatus for producing air-free carbon dioxide on the one hand, and a water-cooled Schiff's nitrometer containing potassium hydroxide on the other. After adjusting the pressure and noting the volume of nitrogen, a solution of iron in concentrated hydrochloric acid is introduced and the nitric oxide collected.

The process and apparatus are minutely described, but contain no novel features. J. C. W.

**The Estimation of Phosphoric Acid as Magnesium Pyrophosphate. III. The Compound Magnesium Tetra-ammonium Diphosphate.** D. BALAREFF (*Zeitsch. anorg. Chem.*, 1918, 103, 73—78. Compare this vol., ii, 266).—The presence in solution of a large quantity of ammonium chloride when magnesium ammonium phosphate is precipitated affects the purity of the precipitate and the accuracy of the result, which is low if the magnesium chloride is added to the phosphate solution, high if precipitation is carried out the reverse way. The presence of an excess of ammonium ions is likely to favour the formation of the compound  $\text{Mg}[(\text{NH}_4)_2\text{PO}_4]_2$ , but attempts to isolate this substance have failed. The precipitate of magnesium ammonium phosphate obtained from a solution saturated with ammonium chloride is found to be partly insoluble in hydrochloric acid after calcination, the insoluble portion being magnesium metaphosphate, and amounting to 10—17% of the weight of the calcined precipitate. Experiments show that the metaphosphate decomposes slowly when heated with a blast flame, more quickly, however, than the pyrophosphate.

The metaphosphate is probably not formed by the direct decomposition  $\text{Mg}[(\text{NH}_4)_2\text{PO}_4]_2 = \text{Mg}(\text{PO}_3)_2 + 2\text{NH}_3 + 4\text{H}_2\text{O}$ . There is always a certain loss of phosphoric acid, which can be accounted for by the decomposition of magnesium tetra-ammonium diphosphate according to the equation  $\text{Mg}[(\text{NH}_4)_2\text{PO}_4]_2 = \text{MgNH}_4\text{PO}_4 + (\text{NH}_4)_2\text{PO}_4$ . The ammonium phosphate dissociates on heating, part of the phosphoric acid being volatilised, part reacting with pyrophosphate to form metaphosphate.

E. H. R.

**The Estimation of Phosphoric Acid as Ammonium Phosphomolybdate.** A. VILLIERS (*Bull. Soc. chim.* 1918, [iv], 23, 305—306).—The author considers that his method (compare A., 1893, ii, 434), in which the phosphate is precipitated as ammonium phosphomolybdate and weighed as such under definite conditions, is more accurate than that of Clarens (compare this vol., ii, 128).

W. G.

**A New Method of Qualitative Analysis without the Use of Hydrogen Sulphide.** GUSTAV ALMKVIST (*Zeitsch. anorg. Chem.*, 1918, 103, 221—239).—The new method, which is described in detail, can be outlined as follows. The sample is first brought into solution, using aqua regia if necessary, but any residue insoluble in aqua regia need not be filtered off. Potassium hydroxide is added to the solution until its strength is about N, followed by potassium carbonate and hydrogen peroxide, the last to destroy oxalic acid and bring chromium into solution. The metals remaining in solution, forming Group I, are arsenic, antimony, tin, lead, zinc, aluminium, and chromium. All other commoner metals are precipitated, forming Group II, except sodium, potassium, and ammonium, which form Group III.

The solution containing Group I is divided into two parts. One part is reduced with iron and hydrochloric acid, whereby arsenic and antimony are reduced to metal, and eventually to their hydrides, which are identified by distillation, tin to stannous chloride. The second part of the solution is treated with sodium sulphide solution in excess, lead and zinc being precipitated as sulphides, chromium as hydroxide, aluminium remaining in solution as aluminate. The aluminium is precipitated as carbonate by a stream of carbon dioxide, the other elements of the group being identified by usual tests.

The precipitate containing the elements of Group II is dissolved by treatment with nitric acid and hydrogen peroxide. The insoluble portion, including that part of the sample originally insoluble in aqua regia, is worked up by usual methods. The solution is treated with freshly precipitated stannic hydroxide and vaporated to dryness to precipitate silicic, phosphoric, arsenic, and antimonious acids, and again extracted with nitric acid. The acid solution is then made strongly alkaline and boiled with hydrogen peroxide to precipitate iron, bismuth, and manganese, then ammonium oxalate added to precipitate calcium, strontium,

and barium. The combined precipitates are evaporated with acetic acid, when calcium, strontium, and barium dissolve as acetates, iron, bismuth, and manganese being undissolved. The individual elements are identified by usual tests.

The filtrate from the iron-barium precipitates contains silver, mercury, copper, cadmium, nickel, cobalt, and magnesium. Silver and mercury are precipitated as metal by means of hydrazine sulphate, copper as cuprous thiocyanate, and the remaining metals detected by special tests.

The method does not claim to effect complete separations of the different groups, but it is efficient for the qualitative detection of the common elements. The modifications of procedure necessary when acid radicals are present which may lead to the formation of complex metallic compounds are described in detail. E. H. R.

**Sulphide Precipitation of Group 2a Metals.** JOSEPH SHIBKO (*Chem. News*, 1918, 117, 253—254).—When these metals are precipitated from a slightly acid solution of a brass or bronze by ammonium sulphide instead of hydrogen sulphide, the precipitate contains small quantities of zinc. [See also *J. Soc. Chem. Ind.*, 517A.] C. S.

**Petersen's Method for the Qualitative Separation of the Cations of the so-called Third and Fourth Groups.** IWAN BOLIN and GUNNAR STARCK (*Zeitsch. anorg. Chem.*, 1918, 103, 69—72).—A number of modifications of Petersen's process (A., 1910, ii, 654) are suggested. After precipitating the metals of the second group with hydrogen sulphide, Petersen precipitates strontium and barium with sulphuric acid. Instead, the authors use sodium sulphate. The precipitate is washed with hot water and the washings are tested for calcium with ammonium oxalate. The residue is then ignited with a little pure carbon, dissolved in 4N. acetic acid and examined for barium and strontium in the usual way. The authors prefer reduction with carbon to fusion with sodium carbonate.

In the separation of chromium from a mixture of iron, manganese, chromium, calcium, and magnesium hydroxides, it is better to oxidise the chromium to chromate with sodium hypochlorite. When sodium peroxide is used, it cannot be completely washed from the residue, and on acidification the hydrogen peroxide formed reduces manganese dioxide, and the manganese, passing into solution with calcium and magnesium, is precipitated with the latter.

For detecting zinc in the group of metals precipitated by sodium sulphide, the precipitate is boiled with alkaline sodium hypochlorite, zinc and chromium passing into solution. The solution is acidified with acetic acid, the chromate precipitated with barium chloride, and the filtrate tested for zinc with ammonium sulphide.

In presence of oxalic acid, the test for aluminium always fails.

Oxalic acid, if present, should be destroyed by boiling with 3% hydrogen peroxide and sulphuric acid. The Petersen process, with these modifications, gives very satisfactory results. E. H. R.

**Estimation of Magnesia in Water.** M. MONHAUPT (*Chem. Zeit.*, 1918, **42**, 338).—The water is neutralised, using methyl-orange as indicator, treated with a quantity of potassium oxalate slightly in excess of the amount of calcium oxide in the water, and a definite excess of *N*/10-alkali solution (prepared by mixing equal volumes of *N*/10-sodium hydroxide and sodium carbonate solutions) is added; the solution is diluted to a definite volume, filtered, an aliquot portion of the filtrate treated with a quantity of calcium chloride equivalent to the oxalate added, and the excess of alkali then titrated with *N*/10-acid. W. P. S.

**Gravimetric and Volumetric Determination of Zinc Precipitated as Zinc Mercury Thiocyanate.** GEORGE S. JAMIESON (*J. Amer. Chem. Soc.*, 1918, **40**, 1036—1039).—Lundell and Bee's method of estimating zinc in alloys as zinc mercury thiocyanate (*Trans. Amer. Inst. Met.*, 1914, 146) is subjected to criticism, the more important being: (1) arsenious compounds need not be removed, and (2) the factor for obtaining the weight of zinc is 0.13115, not 0.1266, since the precipitate, after being dried at 102°—108°, has the composition  $\text{ZnHg}(\text{SCN})_4$ , not  $\text{ZnHg}(\text{SCN})_4 \cdot \text{H}_2\text{O}$ .

Instead of weighing the zinc mercury thiocyanate, a trustworthy volumetric method of estimating the zinc in it is described, based on the reaction  $\text{ZnHg}(\text{SCN})_4 + 6\text{KIO}_3 + 12\text{HCl} = \text{ZnSO}_4 + \text{HgSO}_4 + 2\text{H}_2\text{SO}_4 + 4\text{HCN} + 6\text{KCl} + 6\text{KCl} + 2\text{H}_2\text{O}$ . C. S.

**A New Reaction of Osmium.** I. TSCHUGAEV (*Compt. rend.*, 1918, **167**, 235).—When a solution containing osmium in the form of its tetroxide or as an osmichloride is warmed for a few minutes with thiocarbamide in excess and a few drops of hydrochloric acid, the liquid becomes coloured a deep red or a rose colour, according to the concentration of the osmium. By this means, osmium may be detected at a dilution of 1 in 100,000. The red compound has the composition  $[\text{Os}_6\text{CS}(\text{NH}_2)_2]\text{Cl}_3 \cdot \text{H}_2\text{O}$ , and is thus analogous to the luteo-cobalt salts. W. G.

**New Method for the Rapid Destruction of Organic Matter.** PAUL DURET (*Compt. rend.*, 1918, **167**, 129—130).—The method consists in boiling the material with 10% sulphuric acid and ammonium persulphate until all brown coloration has disappeared, repeated additions of ammonium persulphate being made if necessary. The method is applicable to urines, hair, wool, and also to such substances as sugars, fats, glycerol, and cacodyl compounds. W. G.

**Pregl's Microanalytical Estimation of Methyl Groups attached to Nitrogen.** S. EDLBACHER (*Zeitsch. physiol. Chem.*, 1918, **101**, 278—287).—An account of the difficulties encountered in carrying out Pregl's method, and of various improvements by means of which they have been overcome, the principal being the adoption of a quartz flask instead of one of glass and the addition of a catalyst, gold chloride, which so accelerates the cleavage of the alkyl groups that the whole operation can be completed in one distillation occupying about thirty minutes. H. W. B.

**Reaction of Guaiacol Carbonate. A Test for Ethyl Ether.** G. MAUE (*Pharm. Zeit.*, 1918, **63**, 255—256).—To identify the presence of guaiacol in guaiacol carbonate, 0.02 gram of the latter is dissolved in 1 c.c. of alcohol, 2 drops of ferric chloride solution and 1 drop of formaldehyde solution are added, and 2 c.c. of sulphuric acid are then run in so as to form a layer under the mixture. A cherry-red ring develops at the junction of the two liquids. The test may be used for the detection of aldehydes in ethyl ether; although aldehydes other than formaldehyde do enter into the reaction, the author has found that the aldehydes which may be present in ethyl ether always include some formaldehyde. One c.c. of the ether is mixed with 0.02 gram of guaiacol carbonate, 1 c.c. of water and 1 drop of ferric chloride solution, and 2 c.c. of sulphuric acid are added. Pure ethyl ether for anæsthetic uses should not yield a red-coloured zone (absence of aldehydes); ordinary ether usually gives a reaction with the test. The sensitivity of the test is 1 in 300,000. W. P. S.

**Estimation of Cholesterol in Blood Serum.** ADOLPH BERNHARD (*J. Biol. Chem.*, 1918, **35**, 15—18. Compare Weston, A., 1917, ii, 156).—The new method combines the extraction method of Weston and Kent and the colorimetric method of Grigaut (*Compt. rend. Soc. Biol.*, 1910, **68**, 827). The cholesterol is extracted by a mixture of alcohol and ether (1:1), and an estimation can be completed in five hours. H. W. B.

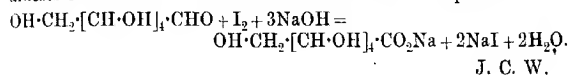
**Cleavage of Digitonincholesteride.** A. WINDAUS (*Zeitsch. physiol. Chem.*, 1918, **101**, 276—277. Compare Lifschütz, this vol., ii, 179).—The author gives further details of his method for the preparation of cholesteryl acetate from digitonincholesteride, but points out that the cleavage is more readily accomplished by the action of hot xylene (Windaus, A., 1910, ii, 462) or by one of the more recent methods, involving the use of acetic anhydride (see Prescher, A., 1917, ii, 275). H. W. B.

**Rate of Production of Colour in Alkaline Solutions of Dextrose and Picrate.** T. ADDIS and A. E. SHEVSKY (*J. Biol. Chem.*, 1918, **35**, 43—51. Compare this vol., ii, 247).—A full account of work previously published. H. W. B.

**Modification of the Picrate Method for the Estimation of Dextrose in Blood.** T. ADDIS and A. E. SHEVSKY (*J. Biol. Chem.*, 1918, **35**, 53—59).—The chief modification consists of the utilisation of a graph showing the increase of intensity of colour corresponding with increase in the concentration of dextrose for correcting the values for the dextrose in blood obtained by the picrate method of estimation. H. W. B.

**Estimation of Dextrose by [Sodium] Hypiodite.** RICHARD WILLSTÄTTER and GUSTAV SCHÜDEL (*Ber.*, 1918, **51**, 780—781).—The dextrose solution is mixed with about twice the amount of 0.1*N*-iodine solution necessary for oxidation to gluconic acid, a quantity of 0.1*N*-sodium hydroxide which is 1.5 times as much as the iodine is slowly added, the mixture is left for twelve to fifteen minutes (or twenty minutes if the proportion of sugar is very small), and then the excess of iodine is titrated after slightly acidifying with sulphuric acid. Taking 10 c.c. of sugar solution, the average error is less than 0.1% with 1% solutions, or less than 1.5% with 0.1% solutions.

Under these conditions, ketoses and sucrose are not affected, and therefore the method will be very useful in the estimation of aldoses in mixtures. The fundamental reaction is expressed thus:



**Detection of Sugar in Urine by means of an Alkaline Copper Solution.** H. RUOSS (*Zeitsch. physiol. Chem.*, 1918, **101**, 193—209).—A modification of the Worm-Müller test is described in which the quantity of the alkaline copper reagent to be boiled with 5 c.c. of the urine depends on the density of the urine. The number of c.c. of reagent required is determined by the formula  $83(D-1) + 0.7$ , where  $D$  is the density of the urine. If a deposit of red cuprous oxide fails to form when the calculated volume of the reagent is mixed with 5 c.c. of urine under the prescribed conditions of temperature and dilution, the urine is normal. By the addition of glycerol to the reagent, its delicacy is greatly increased, so that the presence of dextrose may be detected in even normal urines. H. W. B.

**Estimation of Lactose in Admixture with Sucrose and Invert-sugar.** J. GROSSFELD (*Zeitsch. Nahr. Genussm.*, 1918, **35**, 249—256).—The following formulæ, deduced from the results obtained by experiments with the pure sugars, are given for calculating the quantity of lactose in a mixture also containing sucrose and invert-sugar. The mixed sugars are inverted by heating 50 c.c. of their solution at 100° for thirty minutes with 2 c.c. of hydrochloric acid ( $D$  1.125), and the optical rotation and reducing power of the solution are then determined, the rotation being observed after the solution has remained for twenty-four hours.



Lactose =  $0.01375Z(D + 16.7)$  and sucrose =  $0.01145Z(70.6 - D)$ , where  $Z$  is the total reducing sugar (as invert-sugar) and  $D$  its specific rotation.

W. P. S.

**Detection of Methylpentosans.** KINTARO ŌSHIMA and KINSURU KONDŌ (*J. Tokyo Chem. Soc.*, 1918, **39**, 185—198).—Methylpentosans frequently occur together with pentosans in vegetable substances. In such a case, Ōshima and Tollens's method (*A.*, 1901, ii, 484) for detecting methylpentosans is the most sensitive. If other hydrocarbons of the hexose group are present in addition to methylpentosans and pentosans, the spectroscopic determination of methylfurfuraldehyde in Ōshima and Tollens's method needs some skill, as hydroxymethylfurfuraldehyde derived from hexose will also be found, and its absorption spectrum closely resembles that of methylfurfuraldehyde. The authors describe an improved method depending on the fact that hydroxymethylfurfuraldehyde can be destroyed completely by distillation with hydrochloric acid. Three to five grams of the sample are distilled according to Kröber and Tollens's method (compare *A.*, 1902, ii, 288, 537). When the volume of the distillate reaches 300 c.c., 100 c.c. of it are taken and subjected to a second distillation. When 30 c.c. of liquid have distilled, an equal amount of the first distillate is run into the distilling flask by means of a separating funnel. This procedure is repeated until the whole of the first distillate has been added; the distillation is then continued with additions of hydrochloric acid ( $D$  1.06) in the same manner until the total volume of distillate amounts to 400 c.c. To 5 c.c. of the second distillate, an equal volume of concentrated hydrochloric acid is added, and then a small quantity of a solution of phloroglucinol in hydrochloric acid ( $D$  1.06). After five minutes or more, the precipitate of phloroglucide is filtered off and the absorption band of methylfurfuraldehyde determined in the filtrate.

S. H.

**Sudan III. and the Detection of Fat.** V. H. MOTTRAM (*Proc. Physiol. Soc.*, 1918, xviii—xix, *J. Physiol.*, **52**; from *Physiol. Abstr.*, 1918, **3**, 162—163).—For the detection of fat in physiological mixtures, 1 gram of the powdered solid is shaken with 10 c.c. of a saturated solution of Sudan III in 70% alcohol. The colour of the filtrate is compared with that of the control (1 gram of fat-free starch, etc., similarly treated). If the filtrate is markedly lighter in colour, more than 0.04% of fat is present. For the detection of fat in milk, the curd is treated with acetic acid and filtered; the contents of the filter are treated as above.

S. B. S.

**Estimation of Anthraquinone.** HARRY F. LEWIS (*J. Ind. Eng. Chem.*, 1918, **10**, 425—426).—Anthraquinone mixed with large amounts of anthracene or phenanthraquinone may be estimated by boiling the mixture with an excess of 5% sodium

hydroxide solution and zinc dust; the reduction product is soluble in alkaline solution, and is separated from the insoluble substance by filtration. Re-oxidation occurs when the filtrate is shaken with air, and the resulting anthraquinone is then collected, dried, and weighed.

W. P. S.

**Analysis of Commercial "Saccharin." Estimation of *o*-Benzoylsulphonimide from the Ammonia Produced by Acid Hydrolysis.** H. DROOP RICHMOND and CHARLES ALFRED HILL (*J. Soc. Chem. Ind.*, 1918, **37**, 246—249r).—The various methods available for the analysis of "saccharin" are criticised. It is shown that Reid's hydrochloric acid method (A., 1899, ii, 581) is accurate but rather troublesome. Proctor's method (T., 1905, **87**, 242) tends to low results; it is insufficiently described and leads to discrepancies between analyses. By increasing the time of hydrolysis to four hours or the strength of the acid to 1.5*N*, it becomes trustworthy. The following method is recommended. The "saccharin" is boiled for two minutes with 10 c.c. of 7.5*N*-sodium hydroxide to expel free ammonia, and then for fifty minutes with 15 c.c. of 10*N*-hydrochloric acid, using an efficient reflux condenser. The liquid is cooled and 75 c.c. of cold water are added; 15 c.c. of 7.5*N*-sodium hydroxide are added, and the ammonia is distilled into 20 c.c. of 0.2*N*-hydrochloric acid. The excess of acid is then titrated with 0.1*N*-alkali, using methyl-red as indicator.

J. F. S.

**Identification of the Cinchona Alkaloids by Optical-crystallographic Measurements.** EDGAR T. WHERRY and ELIAS YANOVSKY (*J. Amer. Chem. Soc.*, 1918, **40**, 1063—1074).—Cinchonine, cinchonidine, quinine, and quinidine are separately crystallised from alcohol or benzene, and the crystals are optically examined under the microscope in ordinary light and in parallel and in convergent polarised light; the refractive indices are measured by the immersion method in solutions of potassium mercuric iodide and glycerol of known indices. Tables of the data thus obtained are given. It is shown that the individual alkaloids in a mixture of the four can be identified by the data, and a description is given of the application of the method to the identification of the alkaloids in a medicinal preparation. [See *J. Soc. Chem. Ind.*, 529A.]

C. S.

**Colorimetric Estimation of Brucine in Presence of Strychnine.** A. WÖBER (*Zeitsch. angew. Chem.*, 1918, **31**, i, 124).—The drawback of Dowdard's colorimetric method of estimating brucine in presence of strychnine (P., 1902, **18**, 220) is that the coloration fades with varying velocity according to the concentration of the alkaloid solution. The strong nitric acid used for the reaction also affects the strychnine, producing a yellow coloration. The method may be rendered trustworthy by using a mixture of equal volumes of strong nitric acid (D 1.4) and 20% sulphuric

acid as the reagent, and adding a small amount of a saturated aqueous solution of potassium chlorate immediately after the reaction. The standard brucine solution used for the comparison should contain 0.1 gram of strychnine. [See also *J. Soc. Chem. Ind.*, 441A.] C. A. M.

**Extraction of Nicotine from Aqueous Solutions.** KARL DANGELMAJER (*Chem. Zeit.*, 1918, **42**, 290).—Trichloroethylene is a useful solvent for extracting nicotine from its alkaline aqueous solution; the extraction is quantitative, and the nicotine may be recovered from the trichloroethylene solution by shaking the latter with dilute sulphuric acid. W. P. S.

**Identification of Novocaine.** J. A. SANCHEZ (*Rev. farm. Buenos-Ayres*, 1917, 699; from *Ann. Chim. anal.*, 1918, **23**, 137).—A red coloration is obtained when a 0.2% novocaine solution is heated with 2 drops of 10% sodium nitrite solution and 3 drops of sulphuric acid, then diluted with water and treated with Millon's reagent. This reaction identifies the phenolic nucleus of the substance. The ethylic nucleus is identified by the formation of iodoform, and the aldehydic nucleus by distilling the substance with dilute sulphuric acid and manganese dioxide and testing the filtrate with magenta-sulphurous acid reagent. With bromine, novocaine yields a yellow precipitate, which dissolves when the mixture is heated. W. P. S.

**The Colorimetric Estimation of Hæmoglobin as Acid Hæmatin.** LADISLAUS BERCZELLER (*Biochem. Zeitsch.*, 1918, **87**, 23—35).—By means of an Autenrieth colorimeter, hæmoglobin can be estimated as acid hæmatin, when a washed suspension of corpuscles is employed. The method cannot, however, be employed for determining the amount of hæmolysis in, for example, the Wassermann reaction, as it is interfered with both by the presence of serum and the solution of the antigen in organic solvents. S. B. S.

**Tryptoproteases.** M. FRANCESCO (*Arch. farm. sper. sci. appl.*, 1917, **24**, 3—22; from *Physiol. Abstr.*, 1918, **3**, 165).—From a comparative study of nine methods for determining the presence of trypsin, the author recommends the gelatin method of Fermi as the most delicate and trustworthy. It is fifty times as sensitive as the serum and casein methods for the protease of some of the pathogenic bacteria. S. B. S.

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